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# *The feldspar phenocrysts of some Tertiary acid glasses.*

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*Summary.* The feldspar phenocrysts of some British and Icelandic Tertiary acid glasses have been studied optically and chemically. Six new analyses of the feldspar phenocrysts are presented together with an anorthoclase from a glassy pantellerite. The analysed feldspars and all the other feldspar phenocrysts that have been examined show high-temperature optics, and confirm the results of previous investigations of plagioclase feldspar determinative curves. The relationship of the feldspar phenocrysts to the plagioclase components in the analysed residual glasses conforms to the synthetic plagioclase system, and the crystallization of feldspar in natural acid melts is considered.

SINCE the clear recognition of high-temperature optics of volcanic plagioclases by Kohler (1941, 1942) and Tertsch (1942), little work has been done on the plagioclase feldspars of the British Tertiary volcanic province, although Bradley (1953) has reported that the plagioclase phenocrysts of a pitchstone from Brodick, Arran, have high-temperature optics as may the plagioclase phenocrysts of an Arran felsite. Tuttle and Bowen (1958) have shown the transitional nature of the optics (and the structure) of the plagioclase and alkali feldspars of the Beinn an Dubhaich granite, Skye, as have Emeleus and Smith (1959) for the alkali feldspar phenocrysts of a porphyritic felsite from Slieve Gullion, Northern Ireland. The optical data for the alkali feldspars of the Mourne Mountains granite (G1) given by Brown (1956, table 7) suggest that they also are intermediate between the low-sanidine–anorthoclase and orthoclase–low-albite series (Tuttle, 1952). This paper is concerned with the feldspar phenocrysts of ten pitchstones from the North Atlantic

Tertiary volcanic province, the pyroxene and olivine phenocrysts of which have been separated, analysed, and described (Carmichael, 1960).

Of the ten pitchstones, six come from the east coast of Iceland where they occur in association with the Thingmuli central volcano as an acid dyke (G. 151) and as a pitchstone margin of an acid lava (G. 87): as high-level acid intrusions at Sellatur (E. 868) (Walker, 1959, p. 379), at Bondolfur (P. 186), and at Skruthur (P. 258); and as the chilled margin of a dacitic lava at Rauthaskritha (1C. 3) (Hawkes, 1924). The pitchstones from the British Tertiary all come, with one exception, from the island of Arran, where they form dykes, and have been described by Tyrrell (1928, pp. 210–235). The Arran specimens come from behind the schoolhouse at Brodick (AC. 6), from Glen Shurig (AC. 7), and from the Tormore shore (Judd's No. 1 dyke) (AC. 12). The remaining pitchstone forms the Sgurr of Eigg (EC. 20), which has been described in detail by Harker (1908, pp. 170–174).

The enumeration of the feldspars described here is the same as that of the pyroxenes, olivines, residual glasses, and pitchstones (Carmichael, 1960). Thus, for example, 1*F* is the analysed alkali feldspar (table III), 1*P* the optically determined plagioclase (see below), 1 and 1*A* the analysed pyroxenes, and 1*G* the analysed residual glass, all of which make up the analysed pitchstone (1*R*) that forms the Sgurr of Eigg.

The nomenclature of the high-temperature sodic alkali feldspars has been discussed by Smith and MacKenzie (1958), who have suggested that calcium-bearing alkali feldspars may be distinguished from potassic albite and oligoclase by the presence or absence of a change in symmetry on heating. Unfortunately no X-ray study has been made on these feldspars, nor apparently can a distinction be made by the refractive indices or optic axial angle. However, the development of various twin laws suggests a classification, for four of the analysed feldspars, 1*F*, 4*F*, 7*F*, and 3112*F* (table III and fig. 5), twin only on the Carlsbad, Manebach, and Baveno laws, although very fine shadowy but optically indeterminate lamellar twinning is persistent. The three feldspars 2*F*, 6*F*, and 8*F* (table III and fig. 5) twin on the above laws and also on the albite, albite-Ala, and Carlsbad-albite laws, and very fine lamellar twinning is rare or absent. The feldspars that twin on the complex laws (2*F*, 6*F*, and 8*F*) are for the purposes of this study called plagioclases, whereas the remainder are alkali feldspars, and either sanidine or anorthoclase according to their symmetry. Both the plagioclases and the sodic alkali feldspars as defined here fall into the corresponding

composition fields of high-temperature plagioclase and anorthoclase suggested by Smith and MacKenzie (1958, fig. 1).

*Petrography.*

It is hoped to publish a more detailed account of the petrography of these pitchstones later, so only a very brief summary, mainly concerning the feldspar phenocrysts, is offered here.

The pitchstone of Eigg contains abundant phenocrysts of slightly zoned alkali feldspar (1*F*, table III), together with considerably rarer phenocrysts of augite and orthopyroxene, and opaque iron ores. A dull brown microcrystalline glass with perlitic fracture encloses the phenocrysts. The alkali feldspar may show small and sporadic patches of unmixed sodic feldspar, which is well shown on staining, with very rare crystals having cores of plagioclase. Some of the alkali feldspar phenocrysts have very fine lamellar twinning, which is variable in thickness and extent and is possibly gradational to the clearly developed cross-hatched microcline twinning that may rarely be found bordered by untwinned alkali feldspar. Independent plagioclase is extremely rare, shows well developed lamellar twinning, and has the following optical properties:[1] (1*P*) $\alpha = 1{\cdot}534$ ($An_{12}$), $\gamma = 1{\cdot}543$ ($An_{14}$).

The pitchstone dyke from Tormore, Arran, (AC. 12) contains scattered phenocrysts of slightly zoned plagioclase (2*F*, table III) together with less common ferroaugite and orthopyroxene. The glassy ground mass is pale in colour, and has abundant spiculites, which define the flow banding. The plagioclase phenocrysts are often well rounded, and are twinned on the normal parallel and complex laws. The dyke at Brodick, Arran, (AC. 6) presents a most striking display of scopulites within the glass, which encloses phenocrysts of ferroaugite, olivine, quartz, and weakly zoned plagioclase. The plagioclase phenocrysts, which have not been analysed, have been examined on the universal-stage and the Kohler twin-angle values determined together with the optical constants. As with all the other optically-determined plagioclase phenocrysts, these show high temperature optics:[2] (5*F*) $\alpha = 1{\cdot}538$ ($An_{23}$), $\gamma = 1{\cdot}550$ ($An_{28}$), $2V_{\alpha} = 68°$ ($An_{26}$); U-stage = $An_{26}$.

The Glen Shurig dyke (AC. 7) is the richest in ferromagnesian

[1] The high-temperature plagioclase refractive index and 2V curves of Smith (1958) have been used for this and all subsequent optical determinations.

[2] U-stage = $An_{26}$ refers to the average value of An % of the Kohler twin-angles for the high-temperature plagioclase curves (Tröger, 1956), the abbreviation U-stage being used subsequently.

phenocrysts of all the glasses examined and they consist of olivine, ferroaugite, and xenocrystic orthopyroxene, together with quartz and plagioclase. The plagioclase phenocrysts, which are of variable size, have the following optical properties: (10*F*) $\alpha = 1{\cdot}540$ ($An_{23}$), $\gamma = 1{\cdot}551$ ($An_{30}$), $2V_{\alpha} = 69°$ ($An_{27}$); U-stage = $An_{27}$.

The Icelandic glasses typically have fewer microlites in the glass and are all devoid of quartz as a porphyritic element. Basaltic xenoliths often in advanced stages of digestion are not uncommon, and are particularly frequent in P. 258 and G. 87. The acid lava from Rauthaskritha (1C. 3) contains phenocrysts of plagioclase (9*F*, U-stage = $An_{34}$), olivine, and ferroaugite, all being enclosed in a hyalopilitic glass with rhombs of alkali feldspar (Hawkes, 1924). The acid lava from Thingmuli (G. 87), which rests in the centre of a zone of intense hydrothermal alteration, has well-developed perlitic texture in a pale-coloured glass. Enclosed in the glass are phenocrysts of weakly zoned plagioclase, together with ferroaugite and basaltic material, which may remain coherent or may be scattered throughout the glass as independent minerals. The plagioclase phenocrysts have the following properties: (3*F*) $\alpha = 1{\cdot}546$ ($An_{34}$), $\beta = 1{\cdot}551$ ($An_{37}$), $\gamma = 1{\cdot}554$ ($An_{36}$), $2V_{\alpha} = 79°$ ($An_{34}$); U-stage = $An_{33}$.

The glassy margins of the acid intrusions contain phenocrysts of feldspar together with one or more ferromagnesian silicates and opaque iron oxides. The pitchstone margin of the Sellatur plug (E. 868) has phenocrysts of anorthoclase (4*F*, table III) and ferroaugite, which are enclosed in a pale brown glass. The anorthoclase phenocrysts show a great deal of very fine twinning, often cross-hatched, but not quite coarse enough for optical determination. The well flow-banded pitchstone (P. 186) has phenocrysts of plagioclase (8*F*, table III), together with less abundant ferroaugite and olivine, enclosed in a pale brown glass. The plagioclase phenocrysts are twinned on the normal, parallel, and complex laws, and the very fine twinning characteristic of many of the anorthoclases is not noticeably present. Weakly birefringent spherulites are abundantly developed in P. 258 and may surround many of the phenocrysts of anorthoclase (7*F*, table III) and ferroaugite. The feldspar phenocrysts show extremely fine twinning, which is usually optically indeterminate and which may be cross-hatched. Extremely rare olivine and microphenocrysts of opaque iron oxides are contained in a pale brown glass with well developed perlitic structure.

The Thingmuli acid dyke (G. 151) has phenocrysts of plagioclase (6*F*, table III), which are the most strongly zoned of all the analysed

feldspars, with a probable range of about 6 % anorthite. The contiguous twin lamellae of this plagioclase are sometimes of different composition, and gave consistently large triangles of error for the twin axes (cf. Game, 1957, p. 663). Olivine and ferroaugite, together with the plagioclase phenocrysts, are set in a glassy microlitic groundmass with abundant tiny feldspar laths.

All the feldspar phenocrysts are extremely fresh, and with the exception of no. 6*F* only slightly zoned. No study has been made of the habit of the phenocrysts, but the feldspars vary in habit from the slender laths typical of many of the plagioclase phenocrysts to the stumpier, almost equi-dimensional habit of some of the alkali feldspars.

TABLE I. Modal analyses (vol. %). For the key to these analyses, see below.

| *No.* | *Glass* | *Plagioclase* | *Alk. feldspar* | *Quartz* | *Pyroxene* | *Olivine* | *Iron oxides* | *Basaltic xenoliths* |
|---|---|---|---|---|---|---|---|---|
| EC. 20 (1*R*) | 79·3 | trace | 19·2 | — | 1·0 | — | 0·5 | trace |
| AC. 12 (2*R*) | 97·1 | 2·5 | — | — | 0·2 | — | 0·2 | — |
| E. 868 (4*R*) | 92·0 | — | 6·0 | — | 0·4 | — | 0·4 | 1·2 |
| G. 151 (6*R*) | 89·0 | 8·1 | — | — | 1·6 | 0·7 | 0·6 | — |
| P. 258 (7*R*) | 86·7 | — | 9·2 | — | 0·5 | — | 0·2 | 3·4 |
| P. 186 (8*R*) | 89·6 | 8·9 | — | — | 0·8 | 0·2 | 0·3 | 0·2 |

KEY to TABLES I–V

1*F* Sanidine from Sgurr of Eigg pitchstone (Harker, 1908, pp. 170–174). EC. 20.
1*G* Residual glass from EC. 20.
2*F* Plagioclase (with analysis recalculated after subtraction of 13 % of 2*G*) from Judd's No. 1 dyke, Tormore shore, Arran (Tyrrell, 1928, pp. 218–235). AC. 12.
2*G* Residual glass from AC. 12.
4*F* Anorthoclase from pitchstone margin of Sellatur plug, E. Iceland. E. 868.
4*G* Residual glass from E. 868.
6*F* Plagioclase from glassy margin of dyke, Thingmuli, E. Iceland. G. 151.
6*G* Residual glass from G. 151.
7*F* Anorthoclase from pitchstone margin of intrusion, Skruthur, E. Iceland. P. 258.
7*G* Residual glass from P. 258.
8*F* Plagioclase from pitchstone margin of intrusion, Bondolfur, E. Iceland. P. 186.
8*G* Residual glass from P. 186.
3112*F* Anorthoclase from glassy porphyritic pantellerite, Pantelleria. 3112.
3112*G* Residual glass from 3112.

Analyst: I. S. E. Carmichael. The analyses of the residual glasses nos. 1*G* to 8*G* are taken from Carmichael, 1960 (table VI).

The modal analyses of these porphyritic pitchstones are given in table I, and are slightly different from those given previously

(Carmichael, 1960, table I) as the composition of the feldspar phenocrysts was unknown at that time.

*The optics of the analysed feldspars.*

The refractive indices were determined by the immersion method using sodium light, and care was taken to keep the refractometer at the same temperature as the microscope stage. Although the repeated determinations of refractive index made on different days showed satisfactory precision, it is not believed that the determined values are more accurate than $\pm 0{\cdot}002$. A comparison of the refractive indices of the analysed plagioclases (2*F*, 6*F*, and 8*F*, table III) with the high-temperature curves published by Smith (1958, fig. 3) shows satisfactory agreement, especially if allowance is made for the higher Or content of these plagioclases by recalculating their composition to mol. % An/(An+Ab). This new refractive index data therefore lends support to Smith's suggestion (1958, p. 1190) that the refractive index curves of Schwarzmann (1956) for the high-temperature sodic plagioclases are too low.

The refractive indices of the alkali feldspars are, with the exception of 3112*F*, anomalous. All three indices of 4*F* and 7*F* (table III) are above those of the most sodic of the alkali feldspars (Tuttle, 1952) and an approximate idea of their An content may be derived from the high-temperature plagioclase curves of Smith (1958). The refractive indices of 3112*F* are appropriate to an alkali feldspar of that composition (table III), and the low lime content is similar to that of the high temperature alkali feldspars used for the refractive index variation curves (Tuttle, 1952). As the refractive indices of 1*F* (table III) are comparable with, and lie within the experimental error of, the refractive indices of 3112*F* (table III) it would seem probable that the unusually high content of lime in 1*F* (and in 4*F* and 7*F*) is responsible for the otherwise anomalously high refractive indices (Tuttle, 1952, p. 559). Until the exact structural state of these alkali feldspars is known, they cannot reliably be used for optical determinative curves, but eventually the optical properties of the high-temperature calcic anorthoclases and potassic plagioclases will have to be drawn on a ternary feldspar diagram.

The optic axial angle of all the feldspar phenocrysts was measured directly on a Leitz 4-axis universal stage using the orthoscopic procedure, for many feldspars have noticeable dispersion, and the final setting was made using a yellow optical filter. The average value and the range of 2V is given in table III. The range in values for 1*F* may indicate that it is intermediate between the low-sanidine–high-albite and orthoclase–

low-albite series (Tuttle and Bowen, 1958; Emeleus and Smith, 1959), whereas the variation in 2V of 6*F* (table III) is caused by zoning over a range of about 6 % An.

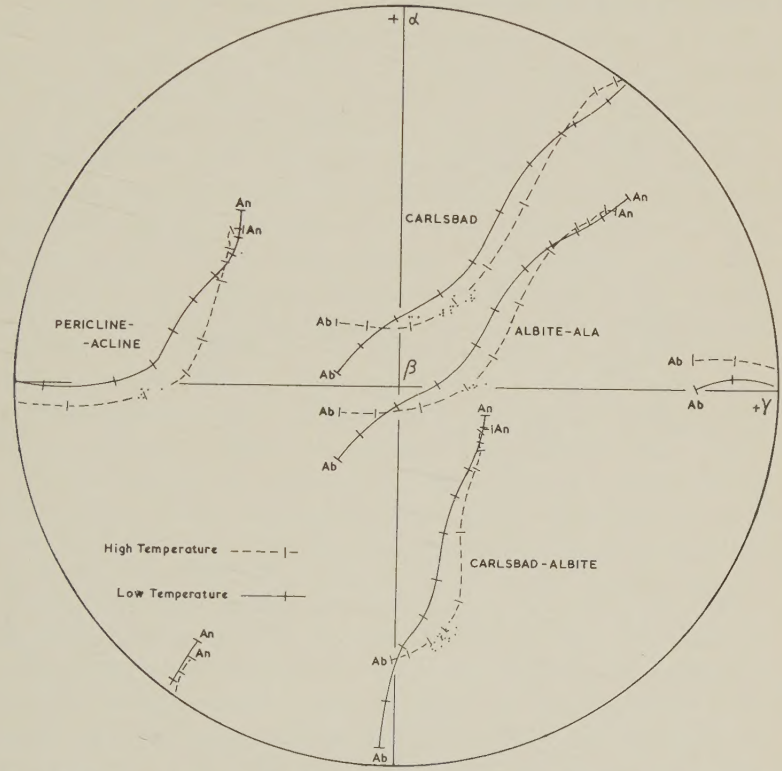


FIG. 1. Stereogram showing the migration of twin-axes of parallel and complex twin laws with change in composition for high- and low-temperature plagioclases. The twin axes of the plagioclase phenocrysts of these acid glasses are plotted.

The average figure for 2V of the analysed plagioclases shows satisfactory agreement with the high-temperature plagioclase values of Smith (1958, fig. 2), whereas the alkali feldspars, with the exception of 3112*F*, are again anomalously high. It is presumed that the high content of lime has had similar influences on the optic axial angle and on the refractive indices of the alkali feldspars (cf. Tuttle and Bowen, 1958, p. 108).

The orientation of the indicatrix with respect to the crystallographic directions of the feldspar phenocrysts was determined by the Fedorov

method on twinned crystals, using the twin axes of the various twin-laws. The crystallographic directions are not precisely obtained from the cleavages, and the commonly vicinal twin composition planes are of little use for precise determination.

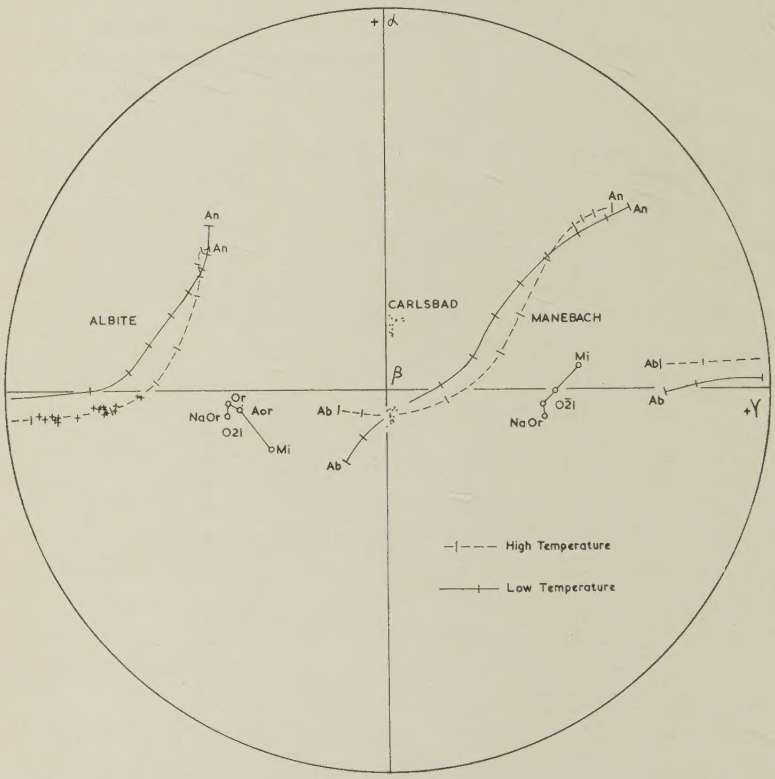


FIG. 2. Stereogram showing the position of the twin-axes of the alkali feldspar phenocrysts (dots) together with the albite twin-axes of the plagioclase phenocrysts (crosses).

The optical directions of both members of a twinned crystal were plotted stereographically, the twin-law identified, and the position of the twin axis after rotation of $\beta$ to the centre of the stereogram determined. The position of the transposed twin-axis enables the composition of a plagioclase to be determined, using the migration curves of van der Kaaden (1951), published by Tröger (1956). The migration curves for the various twin-laws for the high-temperature plagioclases are displaced from the corresponding migration curves for the low-temperature

plagioclases, and it may be seen (figs. 1 and 2) that the twin axes of the plagioclase phenocrysts of these acid glasses all fall on or near the high-temperature migration curves. The average position of the twin axes of each determined twin-law of the analysed plagioclases (2*F*, 6*F*, and 8*F*, table III) is given in table II. It is suggested that the high-temperature migration curve for the Carlsbad-albite twin-law should be slightly lower, as all the determined twin axes fall below the curve (fig. 1). The Carlsbad and Manebach twin axes of one plagioclase (8*F*) fall among those of the alkali feldspars, and nearer to the low-temperature plagioclase migration curves than the high-temperature (fig. 1), and is possible that the optical properties of this feldspar are in some measure similar to those of the alkali feldspars. The twin axes of the alkali feldspars scatter around the position of triclinic anorthoclase. All the alkali feldspars show inclined extinction in the zone [010], but 1*F* usually, although not invariably, shows straight extinction indicating monoclinic symmetry, although the average position of the Manebach and Carlsbad twin axes (table II) lies outside the $\alpha$–$\beta$ plane, and points to triclinic symmetry; this of course may be experimental error.

The composition of plagioclase may also be derived optically by the values of the Kohler twin-angles. These are the angles between each axis of the indicatrix of one twin member and the corresponding axis of the indicatrix of the other member, viz the angles $\alpha\alpha'$, $\beta\beta'$, and $\gamma\gamma'$ where $\alpha\beta\gamma$ are the indicatrix axes for one member and $\alpha'\beta'\gamma'$ the axes for the other member of a twinned individual. Additional values may be obtained if the positions of the optic axes of both members are plotted. Thus if *A* and *B* are the two optic axes of the first member, and *A'B'* the optic axes of the second member, then three independent values may be obtained, namely *AA'*, *BB'*, and *A'B* (the last being theoretically equal to *AB'*). These twin-angle values for various twin-laws of the analysed plagioclase feldspars are given in table II (2*F*, 6*F*, and 8*F*) and generally correspond with the published high-temperature twin-angles (Tröger, 1956) for plagioclases of similar composition. Few values for *AA'*, *BB'*, and *A'B* for high-temperature sodic plagioclase for some twin-laws have been published, so that comparison is impossible. There is a definite tendency for the twin-angles of the Carlsbad-albite law to give aberrant results, and the values read from the high-temperature curves (Tröger, 1956) may indicate a difference of up to 10 % An from the analysed plagioclase composition.

Although no curves of variation of twin-angles with composition for the alkali feldspars have been drawn, it may be seen that the alkali

TABLE II. Twin angle values $\alpha\alpha'$, $\beta\beta'$, $\gamma\gamma'$, $AA'$, $BB'$, and $A'B$ (see text) for the analysed feldspars. $\lambda$ and $\phi$ are the polar coordinates of the relevant twin-axes, with $+\gamma$ at $\lambda = 0°$ and $\phi = +90°$, and $\beta$ (at the centre of the stereogram) at $\lambda = 0°$ and $\phi = 0°$. All values are the average of between two and eight determinations on different crystals. For the key to these feldspars, see page 591.

Twin law:

| | $\alpha\alpha'$ | $\beta\beta'$ | $\gamma\gamma'$ | $AA'$ | $BB'$ | $A'B$ | $\lambda$ | $\phi$ |
|---|---|---|---|---|---|---|---|---|
| *Albite* | | | | | | | | |
| 2*F* ... | 174° | 37° | 37° | 72½° | 62° | 21° | − 3° | −71½° |
| 6*F* ... | 176 | 40 | 41½ | — | — | — | −2 | −69 |
| 8*F* ... | 171 | 15 | 19 | — | — | — | −4 | −81 |
| *Carlsbad* | | | | | | | | |
| 1*F* ... | 36 | 36 | 2 | 32 | 33 | 59 | +18 | +1 |
| 2*F* ... | 48 | 57 | 30 | 21 | 57 | 82 | +24 | +16½ |
| 4*F* ... | 40 | 41 | 3½ | 36 | 37 | 63 | +20 | +2½ |
| 6*F* ... | 51 | 62 | 32 | 19 | 62½ | 83 | +24 | +18 |
| 7*F* ... | 41 | 41 | 7 | 37 | 38 | 59 | +20 | +4 |
| 8*F* ... | 43 | 43 | 9 | 32 | 41 | 74 | +21 | +4 |
| 3112*F* ... | 34 | 34 | 4 | 32 | 31 | 55 | +16½ | +1½ |
| *Carlsbad-albite* | | | | | | | | |
| 2*F* ... | 131 | 136 | 20 | 114 | 80 | 41 | −65 | +25 |
| 6*F* ... | 132 | 136 | 19 | 114 | 80 | 40 | −66 | +25 |
| 8*F* ... | 136½ | 139 | 15 | 120 | 92 | 38 | −68 | +21 |
| *Manebach* | | | | | | | | |
| 1*F* ... | 15½ | 16 | 3 | 16 | 12½ | 50 | −8 | +1 |
| 4*F* ... | 13 | 12½ | 3 | 11 | 11 | 48 | −6 | +1 |
| 7*F* ... | 12 | 12 | 3 | 11 | 12 | 47 | −6 | +1 |
| 8*F* ... | 12 | 10 | 6 | 10 | 11 | 114 | −5½ | +1 |
| 3112*F* ... | 19 | 19 | 2 | 20 | 20 | 50 | −9½ | +1 |
| *Pericline-acline* | | | | | | | | |
| 6*F* ... | 4 | 46 | 45½ | 60 | 73 | 28 | −2½ | −67 |
| *Albite-Ala* | | | | | | | | |
| 6*F* ... | 3½ | 41 | 41½ | 25½ | 27 | 69½ | +1 | +20½ |

feldspars (1*F*, 4*F*, 7*F*, and 3112*F*, table II) show some variation in these values for the Carlsbad and Manebach twin-laws, so that with further data the twin-angles of the alkali feldspars may possibly be used for the determination of their ternary composition.

### *Chemical analyses.*

The feldspar phenocrysts were separated in the Frantz isodynamic separator and by centrifuging in methylene iodide. It was often quite difficult to separate composite grains of feldspar and glass, but it is

believed that with the exception of 2*F*, the feldspars were at least 98 % pure.

TABLE III. Analyses and optical properties of feldspars. Refractive indices ±0·002, $2V_\alpha \pm 2°$. For the key to these analyses, see page 591.

| | 1*F* | 2*F* | 4*F* | 6*F* | 7*F* | 8*F* | 3112*F* |
|---|---|---|---|---|---|---|---|
| $SiO_2$ ... ... | 64·58 | 61·5 | 66·08 | 60·39 | 65·32 | 63·44 | 66·75 |
| $Al_2O_3$ ... ... | 20·30 | 23·7 | 20·27 | 24·35 | 20·69 | 22·37 | 18·84 |
| $Fe_2O_3$ ... ... | 0·43 | 0·2 | 0·42 | 0·44 | 0·53 | 0·35 | 0·88 |
| FeO ... ... | n.d. | — | n.d. | n.d. | nil | nil | n.d. |
| CaO ... ... | 1·26 | 5·4 | 1·58 | 6·21 | 2·18 | 3·42 | 0·06 |
| BaO ... ... | n.d. | 0·07 | 0·30 | tr. | n.d. | n.d. | 0·08 |
| $Na_2O$ ... ... | 6·06 | 7·9 | 9·11 | 7·70 | 9·14 | 9·17 | 7·41 |
| $K_2O$ ... ... | 7·12 | 1·1 | 2·36 | 0·60 | 2·01 | 0·86 | 6·12 |
| $H_2O+$ ... ... | 0·24 | — | 0·17 | 0·24 | 0·14 | 0·23 | 0·18 |
| $H_2O-$ ... ... | 0·10 | — | 0·11 | 0·09 | 0·11 | 0·09 | 0·09 |
| Total ... ... | 100·09 | 99·9 | 100·40 | 100·02 | 100·12 | 99·93 | 100·41 |
| *Composition* (recalculated to 100 wt. %) | | | | | | | |
| Or ... ... | 42·4 | 6·7 | 14·0 | 3·3 | 11·7 | 5·0 | 36·3 |
| Ab ... ... | 51·5 | 66·5 | 77·4 | 65·6 | 77·5 | 77·9 | 63·2 |
| An ... ... | 6·1 | 26·6 | 7·8 | 31·1 | 10·8 | 17·1 | 0·3 |
| Cn ... ... | — | 0·2 | 0·8 | — | — | — | 0·2 |
| α... ... | 1·525 | 1·541 | 1·533 | 1·543 | 1·529 | 1·537 | 1·525 |
| β... ... | 1·530 | 1·547 | 1·538 | 1·548 | 1·536 | 1·543 | 1·529 |
| γ... ... | 1·532 | 1·550 | 1·541 | 1·552 | 1·539 | 1·546 | 1·530 |
| $2V_\alpha$ av. ... ... | 47° | 72° | 48° | 74° | 41° | 58° | 45° |
| Range of $2V_\alpha$ ... | 45°–52° | 70°–73° | — | 68°–77° | — | 56°–60° | 43°–47° |

Normal semi-micro techniques were used for the analysis of these feldspars (table III), and the minimum material was used so that it would later be possible to determine colorimetrically some of the trace elements. The determination of BaO was made in the filtrate from the lime precipitate after destruction of the ammonium salts; it was precipitated and weighed as barium chromate. Barium was also sought in the ignited lime precipitate, and the amount found (very small) subtracted from the figure for lime. $TiO_2$ and MnO were sought but are absent from all the feldspars. FeO was determined in two feldspars (7*F* and 8*F*) but with a negative result, and the writer concludes that the iron in these feldspars is all trivalent. It is of interest that the iron content of 3112*F* (table III) is very much greater than that of the other feldspars, possibly as a result of the very much higher iron content of the pantelleritic residual glass (3112*G*, table V) compared with the other glasses. The analytical methods for the residual glasses have already been briefly described (Carmichael, 1960).

The atomic ratios of the feldspars on a basis of 32 oxygen are set down

in table IV and show a satisfactory balance. However, the composition (as wt. %) of the feldspars computed from the molecular proportions of $Na_2O$, $K_2O$, and CaO generally give totals of less than 100 %, which may be the result of glass impurity in the analysed specimens.

TABLE IV. Formulae of the analysed feldspars on the basis of 32 oxygens. For the key to these analyses, see page 591.

| | 1*F* | 2*F* | 4*F* | 6*F* | 7*F* | 8*F* | 3112*F* |
|---|---|---|---|---|---|---|---|
| Si ... ... | 11·653 | 10·983 | 11·702 | 10·804 | 11·598 | 11·291 | 11·924 |
| Al ... ... | 4·314 | 4·982 | 4·234 | 5·138 | 4·332 | 4·683 | 3·972 |
| Fe‴ ... ... | 0·065 | 0·021 | 0·064 | 0·064 | 0·064 | 0·043 | 0·129 |
| Ca ... ... | 0·238 | 1·031 | 0·298 | 1·193 | 0·416 | 0·652 | 0·011 |
| Ba ... ... | — | 0·004 | 0·021 | — | — | — | 0·004 |
| Na ... ... | 2·125 | 2·727 | 3·127 | 2·666 | 3·137 | 3·165 | 2·575 |
| K ... ... | 1·648 | 0·258 | 0·532 | 0·129 | 0·448 | 0·192 | 1·395 |
| *z* ... ... | 16·03 | 15·99 | 16·00 | 16·01 | 15·99 | 16·02 | 16·02 |
| *xy* ... ... | 4·01 | 4·02 | 3·98 | 3·99 | 4·00 | 4·01 | 3·98 |

*The residual glasses.*

It is proposed to confine this discussion of the residual glasses to those aspects of their chemistry that are believed to be of importance in the crystallization of feldspar. The analyses of the residual glasses of the pitchstones from which the feldspar phenocrysts have been separated and analysed are set down in table V. With the exception of the residual glass from a pantellerite (3112*G*, table V) the analyses are taken from Carmichael (1960). The relationship of the residual glasses to the analysed pitchstones is shown in fig. 3 (taken from Carmichael, 1960) where the analyses have been plotted in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–$SiO_2$–$H_2O$ together with the quartz feldspar boundary curves under various water-vapour pressures (Tuttle and Bowen, 1958, pp. 54–56). The anomalous position of 3*R* 3*G* (G. 87) (fig. 3) is due to a low content of $K_2O$, which is considered to be the result of subsequent hydrothermal alteration. Although the geological environment of 9*R*–9*G* (IC. 3) (fig. 3) is not well known to the writer, this acid lava may be similarly affected. The residual glass of the pantellerite (3112*G*, table IV) has not been plotted in fig. 3 and its composition is in marked contrast to the other residual glasses but generally typical of other analysed pantellerites (Washington, 1914).

*The relationship of the feldspar phenocrysts to the residual glasses.*

In order to assess whether or not the feldspar phenocrysts are in equilibrium with their respective glasses, the phenocrysts have been

plotted on the synthetic plagioclase solidus (fig. 4) (Bowen, 1913) together with the corresponding plagioclase components of the residual glasses, the feldspar-glass pairs being connected by horizontal tie-lines.

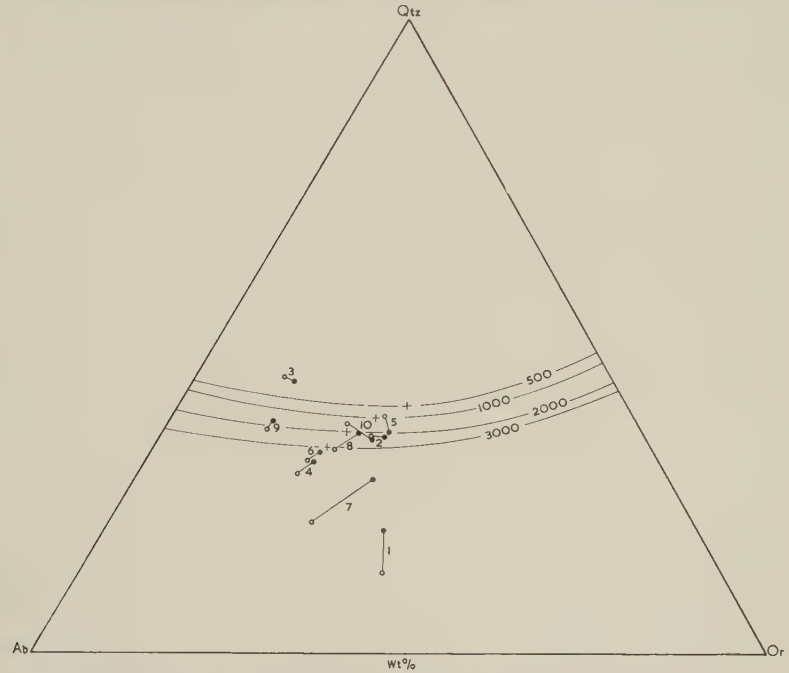


FIG. 3. Normative quartz, orthoclase, and albite of the analysed pitchstones and residual glasses are plotted in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–$SiO_2$–$H_2O$. ○ Analysed pitchstones; ● analysed residual glasses, nos. 1*G*, 2*G*, 4*G*, 6*G*, 7*G*, and 8*G* being presented in table V. The boundary curves for various water vapour pressures (in Kg/cm.$^2$) have been plotted; + indicates position of the minimum on the boundary curves (Tuttle and Bowen, 1958). The diagram is taken from Carmichael, 1960 (fig. 5), as are the rock and residual glass analyses not given here (table V). In the text a pitchstone–residual-glass pair has been referred to as, for example, the pair 3*R*–3*G*.

It may be seen that the plagioclase components of seven of the residual glasses fall very near the synthetic plagioclase liquidus, and it is considered that these phenocrysts are in equilibrium with the plagioclase components of their respective residual glasses. Of the aberrant residual glasses, 3*G* and 9*G* have both been shown to be poor in potash (fig. 3) and the undoubted alteration of one (3*R*–3*G*) suggests the possible alteration of the other (9*R*–9*G*). This deficiency of potash in the residual

TABLE V. Analyses of the residual glasses. For the key to these analyses, see page 591.

| | 1*G* | 2*G* | 4*G* | 6*G* | 7*G* | 8*G* | 3112*G* |
|---|---|---|---|---|---|---|---|
| $SiO_2$ ... ... | 69·4 | 74·0 | 71·5 | 72·3 | 67·0 | 74·2 | 70·1 |
| $TiO_2$ ... ... | 0·59 | 0·14 | 0·22 | 0·22 | 0·55 | 0·19 | 0·41 |
| $Al_2O_3$ ... ... | 14·3 | 11·8 | 12·2 | 12·1 | 12·2 | 11·6 | 7·6 |
| $Fe_2O_3$ ... ... | 1·3 | 0·39 | 0·9 | 0·4 | 1·2 | 0·6 | 2·9 |
| FeO ... ... | 1·0 | 0·84 | 1·7 | 1·4 | 3·9 | 1·0 | 5·6 |
| MnO ... ... | 0·11 | 0·03 | 0·09 | 0·05 | 0·20 | 0·05 | 0·34 |
| MgO ... ... | 0·41 | 0·10 | 0·21 | 0·09 | 0·32 | 0·04 | 0·04 |
| CaO ... ... | 0·92 | 0·62 | 0·62 | 1·0 | 1·4 | 0·71 | 0·53 |
| $Na_2O$ ... ... | 4·7 | 3·9 | 5·0 | 4·9 | 3·9 | 4·3 | 7·1 |
| $K_2O$ ... ... | 5·9 | 4·8 | 3·5 | 3·5 | 4·4 | 4·2 | 4·6 |
| $P_2O_5$ ... ... | 0·10 | 0·02 | 0·02 | 0·04 | 0·11 | 0·04 | 0·05 |
| $H_2O+$ ... ... | 1·4 | 3·6 | 4·1 | 3·8 | 4·3 | 2·8 | 0·23 |
| $H_2O-$ ... ... | 0·2 | 0·1 | 0·1 | 0·1 | 0·1 | 0·1 | 0·04 |
| Total ... ... | 100·3 | 100·3 | 100·2 | 99·9 | 99·6 | 99·8 | 99·8* |
| *Normative feldspar* | | | | | | | |
| Or ... ... | 46·6 | 45·8 | 32·4 | 32·8 | 42·1 | 40·8 | 66·7 |
| Ab ... ... | 53·0 | 53·2 | 66·7 | 65·9 | 53·4 | 59·2 | 33·3 |
| An ... ... | 0·4 | 1·0 | 0·9 | 1·3 | 4·5 | — | — |

* Includes 0·28 % $ZrO_2$.

glasses increases the amount of normative anorthite, and leads to the anomalous composition of the plagioclase components of the residual glasses (fig. 4). No such explanation can be offered for the feldspar glass pair 7*F*–7*G* (fig. 4), as the composition of the pitchstone–glass pair 7*R*–7*G* (fig. 3) is not particularly unusual. Perhaps part of the high content of basaltic material contained in this pitchstone (table I) may have become digested and thus modified the glass composition causing the unusually high content of both iron and magnesia, and perhaps lime (7*G*, table V).

It is of interest to compare the stage of fractionation with respect to the An/(An+Ab) ratio of the feldspar phenocrysts with the stage of fractionation with respect to the $(Fe'' + Fe''' + Mn)/(Fe'' + Fe''' + Mn + Mg)$ ratio of both the olivine and pyroxene phenocrysts. In an account of the ferromagnesian silicate phenocrysts of these acid glasses (Carmichael, 1960) it was suggested that the calcium-rich pyroxene phenocrysts were in equilibrium with the ferromagnesian constituents of the residual glasses, and the phenocrysts and rocks were numbered in all the tables of that account in order of increasing relative enrichment of iron of the calcium-rich pyroxenes, with the exception of no. 10. This same enumeration has been used here, so that, for example, the plagioclase

1*P* (fig. 4) comes from a pitchstone whose pyroxene is the most magnesian of those examined. Thus the numerical order of the feldspar phenocrysts (fig. 4) represents the relative iron enrichment of the pyroxene phenocrysts, and it may be immediately seen that the stage

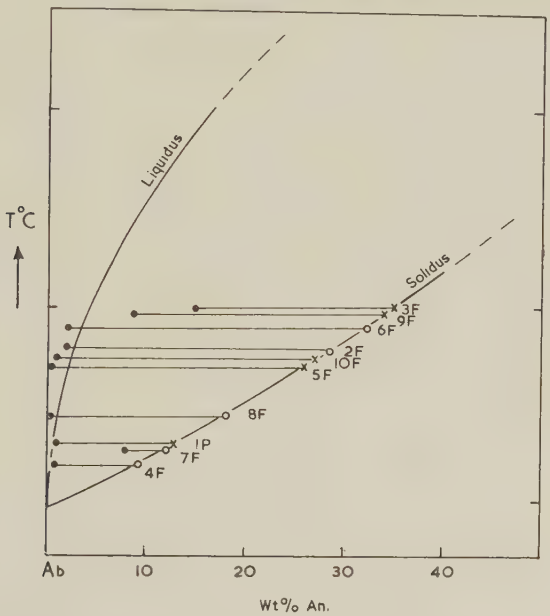


FIG. 4. Part of the synthetic plagioclase diagram (Bowen, 1913) with the feldspar phenocrysts plotted on the solidus and joined to the corresponding plagioclase components of the residual glasses, which lie near the synthetic plagioclase liquidus. ○, analysed feldspar phenocrysts (table III) plotted as weight per cent. An/(Ab+An); ×, optically determined plagioclase phenocrysts; ● normative plagioclase of the residual glasses (table V). The normative plagioclase of the residual glasses for 3*F*, 5*F*, 9*F*, and 10*F* are taken from Carmichael, 1960, table VII. The alkali feldspars 1*F* and 3112*F* (table III) have not been plotted, the optically determined co-existing plagioclase 1*P* being used instead of 1*F*. In the text a feldspar–residual-glass pair has been referred to as, e.g., the feldspar–glass pair 8*F*–8*G*.

of fractionation with regard to the An/(An+Ab) ratio of the feldspar phenocrysts does not correspond with the fractionation stage of the pyroxene phenocrysts. As all the pitchstones with the possible exception of 1*R*–1*G* (fig. 3) have a generally similar chemical composition, and as both the feldspar and pyroxene phenocrysts are believed to be in equilibrium with their glasses, this lack of equivalence of the two

fractionation stages is unusual. In the author's view this may be explained if the temperature of crystallization of either the pyroxene or the feldspar phenocrysts was above the crystallization temperature of the other. This would allow a certain degree of reaction (both the feldspars and the calcium-rich pyroxenes forming continuous solid solution series) of the early formed crystals with the liquid before these crystals were joined by the other member of the pair. The early separation of a calcium-rich pyroxene in varying amounts may cause variation in the $CaO:Na_2O$ ratio of the liquid, so that to a limited extent the anorthite content of a later-separating plagioclase may be controlled by the amount of the calcium-rich pyroxene separating. It is possible that the influence of water in depressing the crystallization temperatures of the pyroxenes and particularly of the feldspars will in some way contribute to or cause the suggested effect. As the temperature of crystallization of the feldspar phenocrysts is unknown and the partial pressure of water also unknown, the temperature scale of the plagioclase system (Bowen, 1913) has been omitted (fig. 4); in this context it may be misleading.

*The crystallization of feldspar in natural acid melts.*

The crystallization of ternary feldspars (An–Ab–Or) in acid melts has been treated in great detail by Vogt (1926, 1931) who examined the coexisting plagioclase and alkali feldspar phenocrysts of acid and subacid rocks, and calculated the composition of the groundmass feldspar. From this and other data, he was able to delineate an 'individualization boundary', which separated the field of potash feldspar from the field of plagioclase. This boundary, later defined as a cotectic by Vogt (1929, pp. 61–64; 1931, p. 225), extended from the Ab-Or sideline (fig. 5) at $Or_{40}Ab_{60}$ to about $Or_{47}Ab_{28}An_{25}$, and then possibly to the An–Or sideline. Bowen (1928) has also discussed the crystallization of ternary feldspars, and Tuttle and Bowen (1958) provide the latest account in which they trace the course of feldspar crystallization using data from the literature on the composition of coexisting plagioclase and alkali feldspar phenocrysts and the host rock or groundmass. This discussion was with reference to trachytic rocks, where, it is suggested, the extent of solid solution of potassium in the plagioclase and of calcium in the alkali feldspars is greatest, the temperature of trachytic crystallization being higher than that of rhyolites or phonolites (Tuttle and Bowen, 1958, pp. 131–137).

The general relationships of the crystallization of ternary feldspar

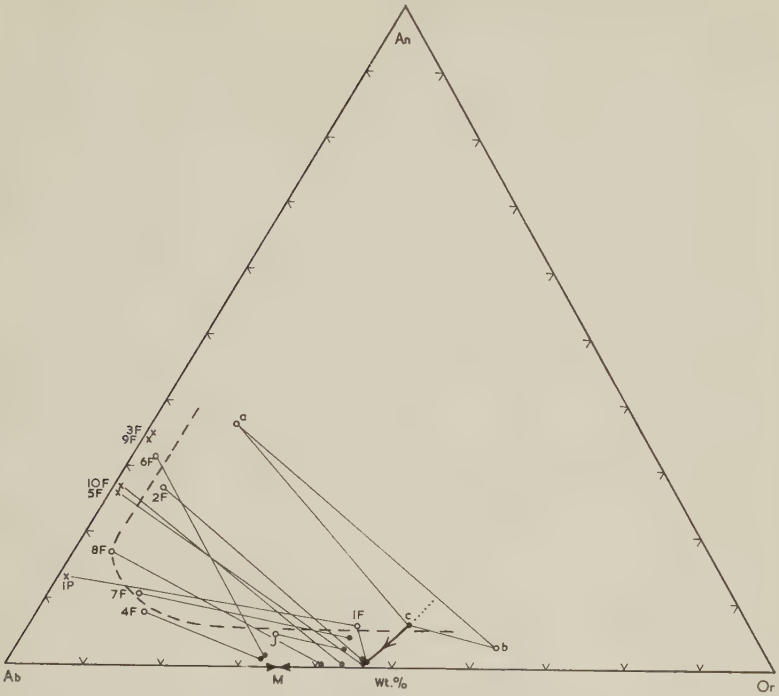


FIG. 5. Ternary diagram of anorthite–albite–orthoclase with the feldspar phenocrysts plotted and joined by tie-lines to their corresponding feldspar components in the residual glasses. ○, analysed feldspar phenocrysts, 1*F* to 8*F* (table III); J, Jafnadal anorthoclase (Hawkes, 1932); *a* and *b*, San Juan plagioclase and sanidine phenocrysts respectively (Larsen *et al.*, 1938, p. 235, table 5, no. 7, and p. 418, table 10, no. SCXX); ×, optically determined plagioclase phenocrysts, all with an unknown potash content; ● normative feldspar components in the residual glasses (table V), the glasses of 5*F* and 10*F* being taken from Carmichael (1960, table VII) and *c* from Larsen and Cross (1956, table 21, no. 48). The Jafnadal anorthoclase is joined to the bulk normative feldspar of the unaltered interior felsite (Hawkes, 1932). – – – possible feldspar solidus; –← feldspar cotectic. *M* is the minimum at 500 kg./cm.$^2$ in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–$H_2O$ (Tuttle and Bowen, 1958). In the text a phenocryst feldspar residual-glass pair is referred to as, for example, the pair 2*F*–2*G*.

deduced by Tuttle and Bowen are applicable to all salic rocks, and are applied here to the porphyritic pitchstones.

The analysed feldspar phenocrysts (table III) have been plotted in the ternary An–Ab–Or diagram together with the feldspathic consti-

tuents of the residual glasses (table V, and fig. 5). A line (dashed) has been drawn through the plotted phenocrysts, and represents the feldspar solidus, which in the case of these acid rocks is displaced towards the Ab corner with respect to the feldspar phenocrysts of the trachytes, and therefore may indicate a lower temperature of crystallization. Intersecting and crossing the solidus is a field boundary (cotectic) which represents the composition of various liquids in equilibrium with both plagioclase and alkali feldspar phenocrysts. The position of this cotectic (fig. 5) has been defined by a San Juan acid residual glass which is in presumed equilibrium with both plagioclase[1] and sanidine, and by the sub-acid residual glass 1*G* (table V), which is in assumed equilibrium with both an alkali feldspar (1*F*, table III) and a plagioclase (1*P*, p. 589). None of the other pitchstones contains two co-existing feldspar phenocrysts and therefore their residual glasses do not lie on the feldspar cotectic. This cotectic (fig. 5) has a different orientation from the one suggested for trachytic rocks by Tuttle and Bowen and in contrast runs to the Ab–Or sideline. Using the data of the feldspar-phenocryst glass relationships (fig. 5) it is possible to generalize on the possible feldspar–liquid equilibrium relations during cooling, the subsequent changes of exsolution and inversion of the feldspars that take place at temperatures below the solidus being neglected. It is assumed that, as the pitchstones have a generally similar composition, the deduced cooling history could be common to them all. It is also assumed that the alkali feldspar solidus does not intersect the underlying solvus.

In tracing a course of crystallization in any phase diagram, it is necessary to know the composition of the initial liquid, which in the case of these porphyritic pitchstones corresponds to the bulk normative ternary feldspar (Carmichael 1960, table VII).

The initial liquids of the pitchstones have been plotted in fig. 6, and with the exception of 3*R* and 9*R*, lie within or very near to the area bounded by the feldspar solidus, the cotectic, the Ab–Or sideline and the Ab–An sideline. The probable alteration of the glasses of 3*R* and 9*R* has already been discussed, and it is believed that originally the bulk normative feldspar would correspond approximately to that of the others, as the abstraction of potash has increased the amount of normative anorthite. It is considered that as the normative bulk feldspar of the unaltered pitchstones falls below the feldspar solidus (fig. 6), all these

[1] Although the plagioclase is assumed here (also Tuttle and Bowen, 1958) to be in equilibrium with the sanidine, Larsen *et al.* (1938, p. 256) have expressed some doubts.

rocks could solidify with a single alkali feldspar, and the possible means of attaining this are discussed below.

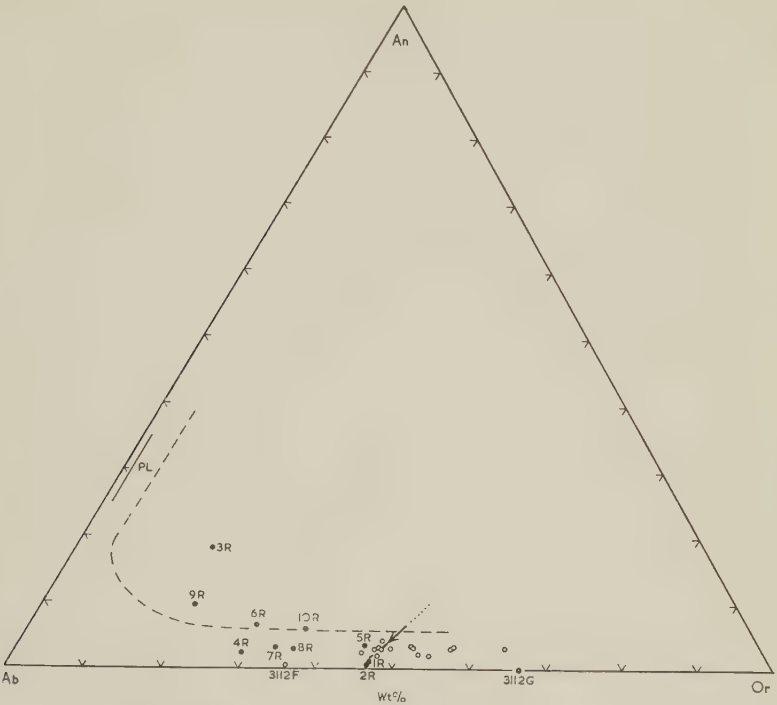


FIG. 6. Ternary feldspar diagram (An Ab Or) with the normative feldspar of the analysed rocks (pitchstones) plotted. ●, 1*R* to 10*R* normative feldspar of pitchstones (Carmichael, 1960, table VII); ○, analysed alkali feldspar phenocrysts of the Slieve Gullion felsite (Emeleus and Smith, 1959, table 2); *PL* is range of optically determined plagioclase phenocrysts of unknown potash content from the Slieve Gullion felsites (op. cit., p. 1189); 3112*F* and 3112*G* are anorthoclase phenocrysts (table III) and residual glass (table V) respectively from glassy pantellerite. – – – feldspar solidus (fig. 5); —<- feldspar cotectic (fig. 5).

A pitchstone liquid on cooling to the temperature of the plagioclase liquidus will start to crystallize a plagioclase feldspar on the solidus, which may contain about 5 % Or (e.g. 2*F* and 6*F*, fig. 5). With further cooling the plagioclase phenocrysts will react with the liquid and moving down the solidus will become more sodic (e.g. 8*F*, fig. 5); the liquid, which continuously reacts with the phenocrysts with falling temperature, will change in composition, and will move on a curved course

(concave to the An corner) towards the cotectic. If at any time the reaction of the plagioclase and the liquid is impeded, plagioclase enclosed by alkali feldspar perhaps in granophyric intergrowth with quartz will result. This texture is typical of many of the Icelandic granophyres. With continued cooling under equilibrium conditions, the plagioclase, moving along the solidus, becomes at once more sodic and potassic, and will lose the distinguishing optical features of plagioclase feldspar and become a sodic anorthoclase (e.g. 4*F* and 7*F*, fig. 5). In the case of liquids represented by these acid residual glasses, the liquid may not yet have reached the cotectic, although the sub-acid liquid of the Eigg pitchstone, which is crystallizing a plagioclase (1*P*, fig. 5) and an alkali feldspar (1*F*, fig. 5), has reached the cotectic a little before the liquids crystallizing feldspars 4*F* and 7*F* (fig. 5); this anomaly may be due to the rather different chemical composition of the Eigg residual glass (1*G*, table V).

Within the temperature interval from the initial crystallization of plagioclase to just above the temperature at which an alkali feldspar may be expected to commence crystallization, the feldspathic composition of the residual glasses (fig. 5) does not seem to change in a consistent direction even though, as noted above, the plagioclase components of the phenocrysts and residual glasses conform to the synthetic system.

Further discussion of the changes on cooling can only be speculative, but the general relationships deduced by Tuttle and Bowen (1958) may again be applied. With a further drop in temperature, the plagioclase may have become more potassic than 4*F* (fig. 5), while the liquid, which has reached the cotectic, begins to precipitate a relatively potassic alkali feldspar. With further cooling, both feldspars continue to react with the liquid, and moving along the solidus, the sodic anorthoclase (original plagioclase) becomes more potassic, and the potassic alkali feldspar becomes more sodic, so approaching one another in composition. Eventually the original plagioclase may completely disappear, and only one alkali feldspar is precipitated. The anorthoclase from Jafnadal, Iceland (Hawkes, 1932), may represent the stage where only one feldspar crystallizes, but unfortunately the composition of the residual glass is unknown, and the phenocryst feldspar is joined (fig. 5) to the composition of the bulk normative feldspar of the unaltered central felsite. It is to be expected that the composition of the Jafnadal liquid will lie nearer the cotectic than is shown. This one-feldspar stage of crystallization may also be represented in some of the Tertiary granite dykes of Skye (Tuttle and Bowen, 1958, tables 17 and 19). However the one-

feldspar margins of the Beinn an Dubhaich, Skye, granite are of alkaline facies and unrepresentative of the original magma (Tilley, 1949).

The two-feldspar porphyritic felsites of Slieve Gullion (Emeleus and Smith, 1959) may represent the two-feldspar stage of crystallization noted above. The higher potash-soda ratio of the host rock (op. cit., table I) and presumably the groundmass (liquid) compared to the pitchstones may place the liquid very near the cotectic so that the two feldspars will begin to crystallize within a smaller temperature interval. The smaller amount of calcium in the alkali feldspars of the Slieve Gullion felsite (fig. 6) suggests that the temperature of crystallization may be lower than that of the porphyritic pitchstones that contain alkali feldspars, whereas the plagioclase phenocrysts of the felsite are considerably richer in lime (fig. 6) than the feldspar deduced to co-exist with an alkali feldspar in the discussion above, under pitchstone conditions of cooling and composition.

In the author's view, the two-feldspar felsites and rhyolites are critical for the elucidation of the crystallization of feldspar in acid melts, for the feldspathic constituents of the groundmass lie on and define a cotectic, and the composition of the phenocrysts may indicate the degree of solid-liquid reaction, which may be considerably different in extent and direction to that suggested here for the feldspar-phenocryst liquid relations of the porphyritic acid glasses.

It is to be expected that an increase in water-vapour pressure will decrease the crystallization temperature of the feldspars, and will also displace the feldspar solidus towards the Ab corner (fig. 5) (Tuttle and Bowen, 1958, p. 135) so that the composition of a single alkali feldspar at the one-feldspar stage of crystallization may vary, although it is considered that a single alkali feldspar while in equilibrium with liquid will conform more or less in composition to that of the minimum in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–$H_2O$ as may the liquids. It is unusual that the anorthoclase phenocrysts from a glassy pantellerite (3112*F*, table III and fig. 6) that have a composition very near that of the minimum should be in presumed equilibrium with a glass (3112*G*, table III and fig. 6) that is so far displaced from the minimum. It can only be concluded that a potential solid phase other than feldspar may take up potash for which biotite seems suited.

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*References*

Bowen (N. L.), 1913. Amer. Journ. Sci., ser. 4, vol. 35, p. 577.
—— 1928. The Evolution of Igneous Rocks. Princeton.
Bradley (O.), 1953. Min. Mag., vol. 30, p. 227 [M.A. **12**-291].
Brown (P. E.), 1956. Geol. Mag., vol. 93, p. 72 [M.A. **14**-71].
Carmichael (I. S. E.), 1960. Journ. of Petrology (in press).
Emeleus (C. H.) and Smith (J. V.), 1959. Amer. Min., vol. 44, p. 1169.
Game (P. M.), 1957. Min. Mag., vol. 31, p. 656.
Harker (A.), 1908. Mem. Geol. Surv. Scotland. The Small Isles of Invernesshire.
Hawkes (L.), 1924. Quart. Journ. Geol. Soc., vol. 80, p. 549.
—— 1932. Min. Mag., vol. 23, p. 163.
Kaaden (G. van der), 1951. Diss. Univ. Utrecht [M.A. **11**-282].
Kohler (A.), 1941. Tschermaks Min. Petr. Mitt., vol. 53, p. 24 [M.A. **8**-313].
—— 1942. Ibid., vol. 53, p. 159 [M.A. **8**-313].
Larsen (E. S.), Irving (J.), Gonyer (F. A.), and Larsen (E. S., 3rd), 1938. Amer. Min., vol. 23, pp. 227 and 417 [M.A. **7**-178].
—— and Cross (W.), 1956. U.S.G.S. Prof. Paper 258.
Schwarzmann (S.), 1956. Heidelberger Beitr., vol. 5, p. 105.
Smith (J. R.), 1958. Amer. Min. vol. 43, p. 1179 [M.A. **14**-284].
Smith (J. V.) and MacKenzie (W. S.), 1958. Amer. Min., vol. 43, p. 872 [M.A. **14**-205].
Tertsch (H.), 1942. Tschermaks Min. Petr. Mitt., vol. 54, p. 193 [M.A. **9**-270].
Tilley (C. E.), 1949. Geol. Mag., vol. 86, p. 81 [M.A. **11**–395].
Tröger (W. E.), 1956. Optische Bestimmung der gesteinsbildenden Minerale. E. Schweizerbartsche, Stuttgart.
Tuttle (O. F.), 1952. Amer. Journ. Sci. (Bowen Volume), p. 553 [M.A. **12**–133].
—— and Bowen (N. L.), 1958. Geol. Soc. America, Mem. 74.
Tyrrell (G. W.), 1928. Mem. Geol. Surv. Scotland. Arran.
Vogt (J. H. L.), 1926. Skrifter Norske Vidensk.-Akad. Mat. Nat. Kl., no. 4 [M.A. **3**–379].
—— 1929. Ibid., no. 6.
—— 1931. Ibid., no. 3.
Walker (G. P. L.), 1959. Quart. Journ. Geol. Soc., vol. 114, p. 367 [M.A. **14**–353].
Washington (H. S.), 1914. Journ. Geol., Chicago, vol. 22, p. 653.

# *The amygdale minerals in the Tertiary lavas of Ireland. IV. The crystal habit of calcite.*

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[Taken as read 2 June 1960.]

*Summary.* Calcite is widespread in amygdales associated with the zeolites; the characteristic forms being {02$\bar{2}$1} and a steep scalenohedron in the zone [$\bar{1}$101], usually {13.11.$\bar{2}\bar{4}$.2}. Crystals from one locality have faces of {16.1.$\bar{1}\bar{7}$.0}, a form new to calcite.

CALCITE is widespread in amygdales and veins in the Antrim Basalts. Broadly, two types of occurrence may be distinguished: a regional type, in which the calcite is associated in amygdales with zeolites in zones of regional extent; and a local type, in which the mineral is one of an assemblage characterizing certain restricted regions in the lavas or is developed in close proximity to faults. These two types of geological environment are reflected by systematic differences in the crystal habit of the calcite. It is the habit of the regional calcite with which this paper is more especially concerned: what might be termed the 'normal' habit of amygdale-calcite, in contradistinction to the 'abnormal' habits of the local categories of occurrence.

Of all the Antrim minerals, calcite shows the greatest diversity of crystal habit, but despite the great variety certain relationships stand out very clearly. The regional calcite, although very variable, is characterized by the presence, and usually the predominance, of one or other or both of *f*{02$\bar{2}$1} and a steep scalenohedron in the zone [$\bar{1}$101], most commonly *W*{13.11.$\bar{2}\bar{4}$.2}. Often these are the only forms developed, but of the others that are found *M*{40$\bar{4}$1}, *r*{10$\bar{1}$1}, and *c*{0001} are the most prevalent. Twinning on *e*{01$\bar{1}$2} is very common, this being practically the only twin-law represented. Of the local occurrences of calcite, that in the plumose-calcite–aragonite–quartz zone in the north-western part of the Antrim Basalts (Walker, 1960) has *e*{01$\bar{1}$2} as the predominant, and often the only, form (there may be a later overgrowth of calcite of 'normal' habit); and the calcite that is so abundant in close proximity to faults, for example in Islandmagee and along the north of the Garron Plateau, often has *v*{21$\bar{3}$1} prominently developed.

*Crystal habit of the regional ('normal') calcite.*

Crystals of steep scalenohedral habit are very prevalent, having been found by the writer at more than 100 localities in the basalts, commonly encrusted by thomsonite. The faces are usually rounded by solution and only rarely can reliable measurements of interfacial angles be made. The steep scalenohedron appears always to belong to the zone $[\bar{1}101]$, easily recognized because the faces show striations parallel to the lateral edges that are parallel to the trace of the $r\{10\bar{1}1\}$ cleavage. The few reliable measurements that have been made indicate that[1] $W\{13.11.\overline{24}.2\}+R12$ is the most abundant of these scalenohedra. Others that have been established as occurring are $\{9.7.\overline{16}.2\}+R8$, $\{11.9.\overline{20}.2\}+R10$, and $\{6.5.\overline{11}.1\}+R11$. Scalenohedra for which measurements were insufficiently reliable to enable the form to be definitely established are $\{32\bar{5}1\}+R5$, $\{7.5.\overline{12}.2\}+R6$, $\{15.13.\overline{28}.2\}+R14$, and a very steep form near $\{31.29.\overline{60}.2\}+R30$. All but the last form are listed in Palache's tables (1940). Curved zones of vicinal faces approximating to steep scalenohedra are common on crystals of this habit. Crystals of rhombohedral habit with $f\{02\bar{2}1\}$ predominant are equally abundant in Antrim, and even more characteristic of the Chalk immediately below the lavas.

The only other study of the habit of calcite in the Antrim Basalts is that by Smith and Ashcroft (1916); they described from Craigahulliar Quarry a crystal of scalenohedral habit with $\{6.5.\overline{11}.1\}$ together with a small face of $\{22.21.\overline{43}.1\}$. Other crystals from the same locality had $\{11\bar{2}0\}$ and small faces of $\{13.11.\overline{24}.2\}$, terminated by $\{10\bar{1}1\}$ and $\{40\bar{4}1\}$. From Whitehead they described crystals with $\{02\bar{2}1\}$ predominant, with $\{04\bar{4}1\}$ and a scalenohedron, $\{35\bar{8}4\}$, lying in a zone other than $[\bar{1}101]$.

One of the best localities for calcite is a quarry almost at the top of the little hill, Baird's Brae, at Roughfort. This quarry was repeatedly visited by the writer over a period of several years, and many thousand calcite crystals seen. Three lava flows are exposed in the quarry, and the red tops of the two lower flows have abundant amygdales up to one or two inches and exceptionally as much as one foot in diameter. These, and sparse veins, contain an abundance of calcite in crystals seldom more than an inch long, and chabazite of habits 3 to 5 (Walker, 1951). Sparse cavities in the interior of the flows contain apophyllite and gyrolite and rare thomsonite and natrolite. A few cavities have been seen containing

[1] The Naumann symbol of the scalenohedron is given following the Miller-Bravais symbol; + R is the rhombohedron of the lateral edges, namely $\{10\bar{1}1\}$, and the figure following gives the intercept on *c*.

TABLE I. Frequencies of scalenohedra in the zone [$\bar{1}101$] of calcite.

| *Miller-Bravais Index* | *Naumann Symbol* | *Frequency (Palache)* | *Antrim: number of localities* |
|---|---|---|---|
| {22.21.$\bar{4}\bar{3}$.1} | +R43 | — | 1 (Smith and Ashcroft) |
| {31.29.$\bar{6}\bar{0}$.2} | +R30 | — | — |
| {21.19.$\bar{4}\bar{0}$.2} | +R20 | 2 | 1 (not established) |
| {9.8.$\bar{1}\bar{7}$.1} | +R17 | 3 | — |
| {17.15.$\bar{3}\bar{2}$.2} | +R16 | 2 | — |
| {8.7.$\bar{1}\bar{5}$.1} | +R15 | 5 | — |
| {15.13.$\bar{2}\bar{8}$.2} | +R14 | 2 | 2 (one not established) |
| {7.6.$\bar{1}\bar{3}$.1} | +R13 | 10–25 | — |
| {13.11.$\bar{2}\bar{4}$.2} | +R12 | 10–25 | 6 (including one by Smith and Ashcroft) |
| {6.5.$\bar{1}\bar{1}$.1} | +R11 | 10–25 | 4 (including one by Smith and Ashcroft) |
| {11.9.$\bar{2}\bar{0}$.2} | +R10 | 2 | 1 |
| {54$\bar{9}$1} | +R9 | 10–25 | — |
| {9.7.$\bar{1}\bar{6}$.2} | +R8 | 5 | 1 (not established) |
| {43$\bar{7}$1} | +R7 | > 25 | — |
| {23.17.$\bar{4}\bar{0}$.6} | +R6⅔ | 1 | — |
| {11.8.$\bar{1}\bar{9}$.3} | +R6⅓ | 4 | — |
| {7.5.$\bar{1}\bar{2}$.2} | +R6 | 3 | 1 (not established) |
| {10.7.$\bar{1}\bar{7}$.3} | +R5⅔ | 7 | — |
| {13.9.$\bar{2}\bar{2}$.4} | +R5½ | 1 | — |
| {19.13.$\bar{3}\bar{2}$.6} | +R5⅓ | 6 | — |
| {32$\bar{5}$1} | +R5 | > 25 | 2 (one not established) |

aragonite and pale green plumose calcite, the quarry lying at the edge of a zone of basalts a few square miles in extent containing the plumose-calcite–quartz–aragonite assemblage. Practically all the calcite crystals seen had either *f* or a steep scalenohedron of the zone [$\bar{1}101$], and the range of habits encountered is illustrated by fig. 1. Some crystals have *f* alone; others have *f* and *W* together; and perhaps the commonest crystals are scalenohedral in habit with *W* terminated by *f*, with or without *M*, or by *r* or *c*. Crystals tabular on *c* are very rare. Characteristic features are the rounding by solution of the faces of *f*; the usually rough condition of *r*, and even more so of *c*, although bright faces of both are seen on occasion; and the generally strong striations on the scalenohedron faces parallel to the lateral edge, striations that are heightened by solution, and some of which may be due to narrow faces of less steep scalenohedra, the faces of which are curved and give multiple reflections. The characteristic scalenohedron is *W*, as is shown by the following measurements[1] made on two crystals:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 65°\,18',\ 65°\,02',\ 65°\,15',\ 65°\,19',\ 65°\,15'$, average $65°\,13'$ (cf. $65°\,10'$ calculated for *W*);

[1] All the measurements were by single-circle goniometer.

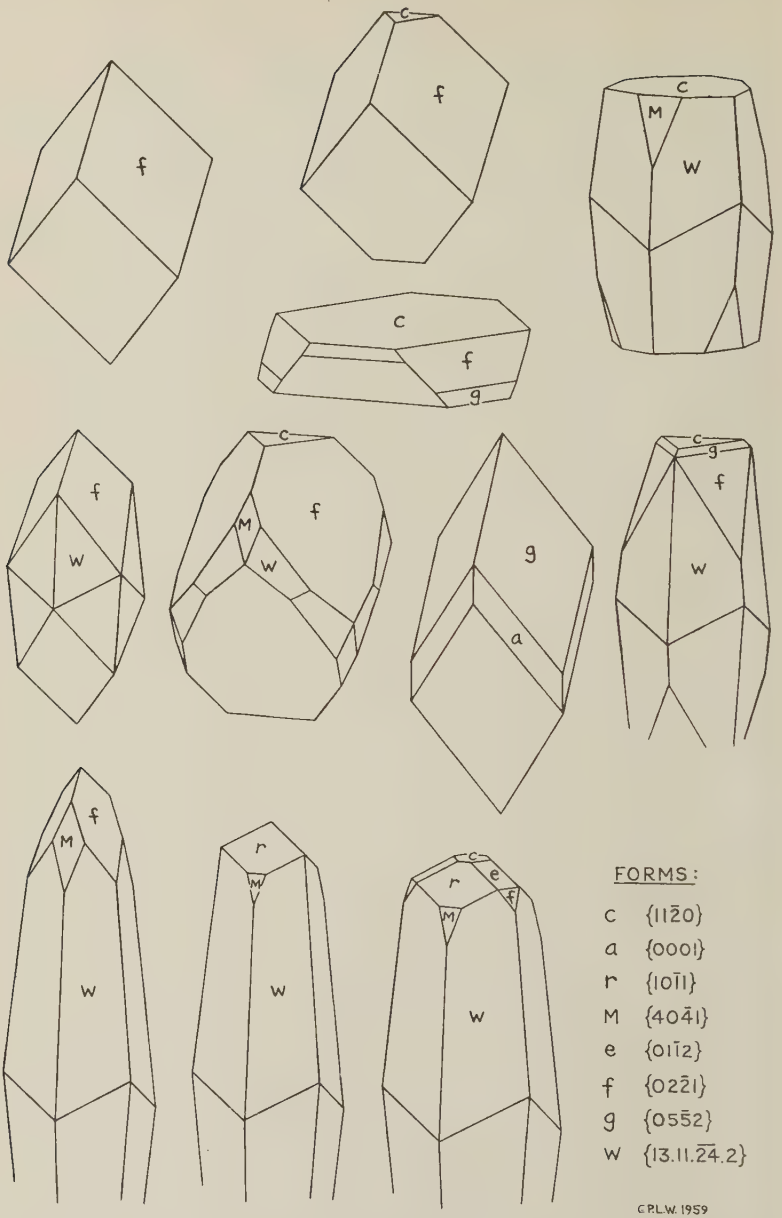


FIG. 1. Calcite habits encountered at Roughfort (Baird's Brae) Quarry.

$(hk\bar{i}l):(i\bar{k}\bar{h}l)$ = 54° 17′, 54° 01′, 54° 03′, 54° 10′, average 54° 08′ (cf. 54° 13′ calculated for *W*).

Little is known of the relative age of crystals of different habits, but some ghost crystals found in one vein had *f* predominant in the core,

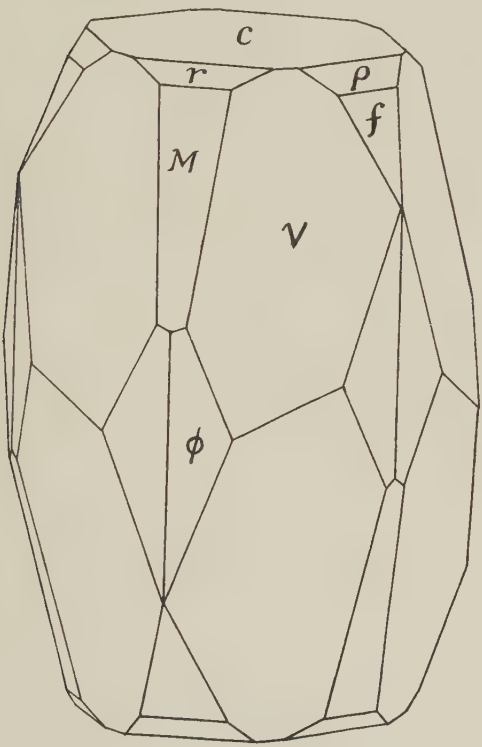


Fig. 2. Calcite from Roughfort showing the new form {16.1.$\bar{17}$.0}.

whereas the later calcite was of scalenohedral habit with *W* predominant. The habits described above are invariably later than plumose calcite, on which *e* is the main form.

A large basalt quarry 0·4 miles NE. of trig. point 607′ on Baird's Brae, Roughfort, has sparse plumose calcite in veins with a parallel overgrowth of calcite of scalenohedral habit. One of the specimens is interesting as bearing a form that is new for calcite, namely the dihexagonal prism {16.1.$\bar{17}$.0}. The crystals that bear this form are short, stumpy, and barrel-shaped (fig. 2) and consist of a steep scalenohedron

terminated by $c$, and with small faces of $M$, $r$, $f$, and probably $\rho\{01\bar{1}1\}$, giving the following interfacial angles:

$c:M = 75° 48', 75° 50', 75° 42'$, average $75° 47'$ (cf. calculated value, $75° 47'$);
$c:r = 44° 44', 44° 40'$ (cf. $44° 36'$ calculated).

The dihexagonal prism forms pairs of very bright faces, slightly striated near their join due to a little oscillatory combination. The faces give perfect signals. Measured values of the angle $(h\bar{l}k0):(k\bar{l}h0)$ are $5° 59', 5° 54', 6° 02'$ for one crystal, average $5° 58'$. Calculated values for this interfacial angle for possible dihexagonal prisms of high index are: $\{13.1.\bar{1}4.0\} = 7° 20'$, $\{15.1.\bar{1}6.0\} = 6° 22'$, $\{16.1.\bar{1}7.0\} = 6° 01'$, $\{17.1.\bar{1}8.0\} = 5° 45'$, $\{19.1.\bar{2}0.0\} = 5° 13'$. These values show that the present prism is most probably $\{16.1.\bar{1}7.0\}$, which is a form new to calcite.

The scalenohedron faces on these crystals are striated and unfortunately give multiple reflections in the zone $[\bar{1}101]$, the peak of the reflections corresponding roughly to $\{7.5.\bar{1}2.2\}+R6$. Scalenohedral crystals from another vein in the same quarry and terminated by $M$ and $f$ show a steeper form; the faces gave exceptionally good signals, and the following angles were measured:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 65° 39', 65° 35', 65° 35'$, average $65° 36'$;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) = 53° 44', 53° 36', 53° 41'$, average $53° 40'$;
$(hk\bar{i}l):(10\bar{1}1)$ cleavage $= 45° 50', 45° 49'$.

These angles agree very well with the calculated values $65° 35'$, $53° 40'$, and $45° 41'$ respectively for $\{6.5.\bar{1}1.1\}+R11$. The same crystals also have faces of a less steep scalenohedron, which is probably $\{9.7.\bar{1}6.2\}$, though the faces did not give very reliable reflections.

Another locality that has yielded much calcite is a large quarry in four basalt flows on the northern slope of Carnmoney Hill, north of Belfast. The amygdales in the flows contain chabazite and thomsonite, with smaller amounts of apophyllite, gyrolite, mesolite, and sparse stilbite. Calcite is abundant in amygdales and in veins accompanying a sharp flexure in the quarry, and it shows considerable habit variation. Most of the crystals found are of steep scalenohedral habit, but many show $f$ alone or predominant. The faces of this form are very readily dissolved, and this often leads to the development of a flat solution scalenohedron. Unusually interesting were crystals, found in a vein some years ago, of a rhombohedron, $\{03\bar{3}2\}$, closely simulating a cube.

The calcite at this locality illustrates a feature often encountered in the Antrim crystals: when it occurs in veins, the crystals are very commonly twinned on $e\{01\bar{1}2\}$. In many veins all of the crystals are twinned, and have the characteristic platy habit due to infilling of the re-entrant angle of the twin. Such twinning is confined to the calcite of veins, being never found in amygdales, and it seems likely that twinning was initiated by stress during growth of the crystals.

A few crystals suitable for measurement were collected from basalt lavas on the shore at Heddles Port, Islandmagee. The crystals show a steep scalenohedron, the faces of which give excellent reflections, and the following interfacial angles were measured on three crystals:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) - 65° 07', 65° 07', 65° 31', 64° 53', 65° 34'$, average $65° 12'$;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) - 54° 16', 53° 49', 54° 18', 53° 57', 54° 21', 54° 23', 53° 57'$, average $54° 09'$.

These values agree well with the calculated values of $65° 10'$ and $54° 13'$ respectively for $W$.

Several small crystals from the Middle lava series of Bengore Head show a steep scalenohedron terminated by various combinations of $r$, $f$, and $M$. All but $f$ gave good reflections, and the following angles were measured on one crystal for the scalenohedron:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 65° 25', 65° 08', 65° 28'$, average $65° 20'$;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) = 53° 53', 54° 08', 54° 05'$, average $54° 02'$;

these again agree well with the calculated values for $W$.

In a large basalt quarry beside the railway in the glacial overflow channel 3 miles east of Ballymoney most of the calcite is a dull grey plumose variety in which $e$ is the predominant form. Minute brilliant crystals formed as a parallel overgrowth on a substratum of plumose calcite are stumpy scalenohedral in habit, terminated by $M$, $f$, and other forms. The following angles were measured on one crystal:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 65° 30'$;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) = 53° 33', 53° 37'$, average $53° 35'$.

These values agree well with the calculated values $65° 35'$ and $53° 40'$ respectively for $\{6.5.\bar{11}.1\}+\mathrm{R}11$. There is also present a less steep scalenohedron in the same zone with $(hk\bar{i}l):(kh\bar{i}\bar{l}) = 30° 47'$, indicating probably either $\{32\bar{5}1\}$ or $\{17.11.\bar{28}.6\}+\mathrm{R}4\frac{2}{3}$, for which the corresponding calculated angles are respectively $29° 16'$ and $31° 18'$.

Large cavities in basalt in a quarry a short distance east of Portadown contain brown calcite with *f* modified by a steep scalenohedron. Measured angles for this scalenohedron are:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 64° 00'$;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) = 55° 06'$.

These values may indicate $(15.13.\overline{28}.2)+$R14 for which the corresponding calculated angles are respectively 64° 28′ and 55° 04′; the reflections are not good enough to enable this form to be established.

Zeolites (faröelite, chabazite, and a little stilbite) follow the brown calcite at this locality, and are followed in turn by colourless calcite of steep scalenohedral habit, terminated by *r*, *f*, and *M*. One brilliant crystal, of stumpy scalenohedral habit, gave the following measured values:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 65° 12', 65° 15', 65° 08'$, average 65° 12′;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) = 54° 13', 54° 11', 54° 08'$, average 54° 11′;
$(hk\bar{i}l):(kh\bar{i}\bar{l}) = 12° 26'$.

These agree well with the calculated values 65° 10′, 54° 13′, and 12° 27′ respectively for *W*. The lateral edges of the scalenohedron are bevelled by brilliant faces of $a\{11\bar{2}0\}$. On another crystal of similar habit the short terminal edges of *W* are bevelled by bright faces of a rhombohedron that must be $\{09\bar{9}1\}$.

Crystals collected from the shore west of Kinbane Head show a steep scalenohedron for which the following angles were measured (the faces gave rather diffuse reflections, but the values first cited are probably reliable):

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 65° 53', 65° 46', 66° 03'$, average 65° 54′;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) = 53° 07', 53° 15', 53° 31'$, average 53° 18′.

These values agree well with the calculated values 66° 07′ and 53° 00′ respectively for $\{11.9.\overline{20}.2\}+$R10.

Crystals from a quarry at the western end of Keady Mountain show a steep scalenohedron terminated by *r* and *M*. Measured angles for the scalenohedron are:

$(hk\bar{i}l):(\bar{h}i\bar{k}l) = 61° 37'$;
$(hk\bar{i}l):(i\bar{k}\bar{h}l) = 56° 25'$;
$(hk\bar{i}l):(kh\bar{i}\bar{l}) = 49° 12'$ to 50° 22′.

These values agree roughly with the scalenohedron $\{21.19.\overline{40}.2\}+$R20,

but the crystals are not good enough to enable this form to be established.

Brilliant crystals of acute scalenohedral habit from a quarry ½ mile south-east of Ballyclare gave reliable measurements indicating the scalenohedron to be $\{13.11.\overline{24}.2\}+R12$. Two minute crystals from the Langford Lodge borehole[1] were also measured; a single measurement on one incomplete crystal of scalenohedral habit from a depth of 880 ft. indicates $\{15.13.\overline{28}.2\}+R14$ as the scalenohedron present, and a crystal from 1350 ft. has $\{6.5.\overline{11}.1\}+R11$ as the predominant form.

*Discussion.*

It is quite clear from the measurements that several steep scalenohedra in the zone $[\bar{1}101]$ are represented in Antrim. Unfortunately measurable crystals are very scarce in Antrim, and it is reasonable to suppose that as the number of measurable crystals is increased so the number of scalenohedra established would likewise increase. Calcite is readily dissolved by meteoric waters, and most of the crystals collected by the writer have been dissolved to some extent; the scalenohedron faces give multiple reflections, and measurement is useless. A list of known scalenohedra in the zone $[\bar{1}101]$ steeper than $+R5$ is given in table I together with Palache's (1940) data on the frequency (the number of localities from which the form has been recorded).

Crystals of steep scalenohedral habit are so common and characteristic of the regional type of occurrence in Antrim that one is prompted to inquire if this habit may be typical of basaltic regions elsewhere. The limited available data in the literature does not lend much support to the idea that they are. For example, of the sixty illustrations of calcite from the Tertiary basaltic region of the North Atlantic in Goldschmidt's Atlas (1913) only three (fig. 1002 from the Faröes; figs. 2001 and 2 from Skye) are of this habit. On the other hand, the writer's observations in the Tertiary basalts of eastern Iceland suggest that in fact the Antrim type of habit is very widespread. The reason why this habit is so poorly represented in the literature is probably that crystals with the regional type of occurrence are rather small and inconspicuous; where calcite is most abundant and conspicuous it is in a geological environment of the local type. Thus the well-known Helgustadir Iceland Spar deposit is situated in altered basalts within an aureole of intense hydrothermal alteration about a Tertiary volcanic centre (Walker, 1959).

[1] The writer is indebted to the Director of the Geological Survey of Northern Ireland for permission to examine specimens and to publish this note.

The basic uniformity in habit throughout the normal zeolite zones of the Antrim Basalts presents further evidence that crystal habit is not due to chance, but is controlled by the conditions obtaining at the time of crystallization. Exactly what those conditions were in the case of Antrim cannot at present be deduced, but the conditions must have been similar to those under which zeolitization took place, for the regional type of calcite is usually associated with zeolites and commonly precedes them in amygdales. Goldschmidt illustrates calcite of similar steep scalenohedral habit from a number of localities, notable from Andreasberg and Zellerfeld in the Harz, and from Framont in Belgium, which suggests that similar conditions may obtain elsewhere than in basic lavas. One must suppose that the various steep scalenohedra require closely similar conditions for their formation.

*References.*

Goldschmidt (V.), 1913. Atlas der Krystallformen, pt. II.

Palache (C.), 1943. Contrib. Dept. Min. & Petr., Harvard Univ., No. 259.

Smith (G. F. H.), Ashcroft (F. N.), and Prior (G. T.), 1916. Min. Mag., vol. 17, p. 274.

Walker (G. P. L.), 1959. Quart. Journ. Geol. Soc., vol. 114, p. 379.

—— 1960. Min. Mag., vol. 32, p. 503.

# *The unique meteorite crater at Dalgaranga, Western Australia.*

By H. H. Nininger, D.Sc., and Glenn I. Huss, A.M.

American Meteorite Museum, Sedona, Arizona.

[Read 3 November 1960.]

*Summary.* The first scientific examination of the Dalgaranga crater has revealed specimens exhibiting a variety of structures and compositions hitherto unknown in connexion with any meteorite crater. Excavations have yielded much-weathered specimens and permitted measurements of the form and depth of the original pit. The question of age is considered, and the impacting meteorite is thought to have been largely stony but at least in part a mesosiderite.

UP to the time of our first visit in 1959, this beautifully shaped, well-preserved but obscure little crater had received only slight mention in scientific literature. So slight mention, in fact, that when we inquired after its whereabouts at the Western Australian Museum in Perth, no one knew where it was located. It took a quick letter home to locate the only written reference to the Dalgaranga meteorite crater known to us.

In December 1938 the late Dr. Edward S. Simpson, Government Mineralogist and Analyst for Western Australia, had published a brief account of a meteorite crater located on the Dalgaranga Station,[1] together with the description of a 42-g. nickel-iron meteorite fragment which reportedly came from its vicinity. He credited Mr. G. E. Willard, former manager of the Dalgaranga Station, as his source of information, and relied upon Willard's observations for his description of the crater.

Willard reported that he had first seen the crater in 1923, but that it had been formed before 1910. Its dimensions he gave as 225 ft. in diameter and 15 ft. in depth. Numerous specimens had been picked up around the crater, he said, but he could provide Dr. Simpson with only the one 42-g. fragment. The others presumably had been lost.

Dr. Simpson's report became the basis for the description of the Dalgaranga Crater and meteorite (classified as a medium octahedrite) that appeared in Dr. M. H. Hey's 1953 revision of the Catalogue of Meteorites

[1] Min. Mag., 1938, vol. 25, p. 157.

issued by the British Museum (Natural History). From there, the statistical description of the crater found its way into other publications without further investigation. A visit to this crater was, therefore, an important item on the agenda of an expedition to the Orient and Australia undertaken by members of the American Meteorite Museum staff in the winter of 1958–59.

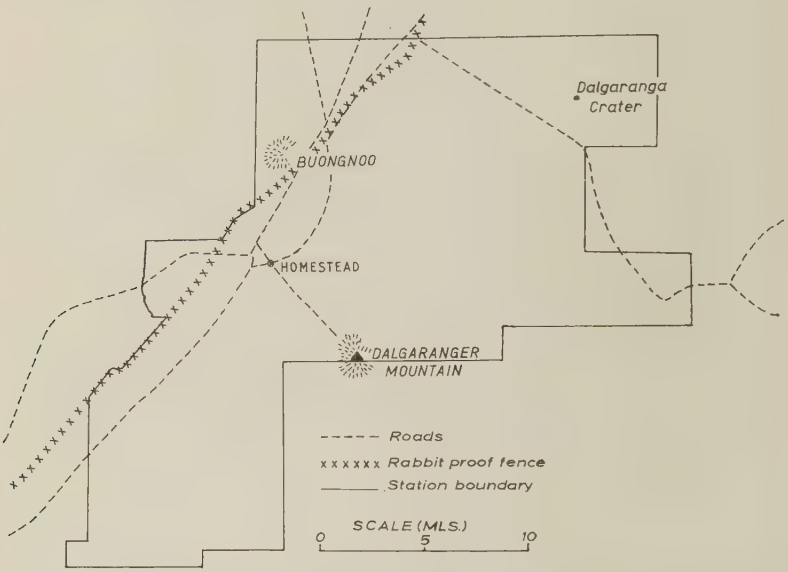


FIG. 1. Dalgaranga Station (27° 45′ S., 117° 5′ E.) and meteorite crater. The homestead is about 50 miles north-east of Yalgoo, Western Australia.

In February 1959 our party, composed of Dr. and Mrs. Nininger and Mr. Allan O. Kelly, set out from Perth, Western Australia, to drive to the town of Yalgoo, from which point we hoped to reach the Dalgaranga Station and visit the crater. Yalgoo is about 400 miles north-north-east of Perth on the Geraldton–Mt. Magnet road, and is a remnant of a once-prosperous mining town. Mr. Jack L. Nevill, a local resident, was most co-operative in directing us to the Dalgaranga Station; he knew of the crater and had seen several small specimens of iron meteorites from it, but had never seen the crater itself.

The Dalgaranga Sheep Station is a small one by Western Australian standards, comprising about 260 000 acres. It is in a region of slight rainfall that supports a rather open stand of mulga and other small trees—typical Western Australian 'bush'. The terrain is largely decayed

granite with a more or less prominent layer of laterite. The crater is about 26 miles by track from the Station headquarters; our attempt to find it by verbal directions ended in confusion, but Mr. C. H. Ross, the Station manager, and an aborigine employee led us to the spot with little difficulty. We set up camp near the crater rim and remained two days.

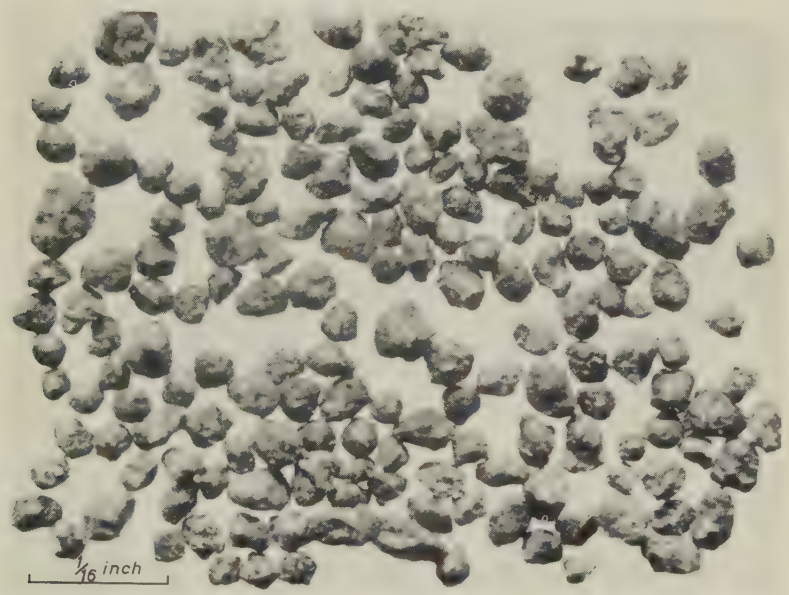


Fig. 2. Metallic spheroids from the Arizona meteorite crater. The particles are 60 % nickel-iron (17·3 % Ni) surrounded by an oxide crust.

It was immediately evident that the published description of the crater was in error, and crude measurements at once lent support to our suspicion that 'feet' had been changed to 'yards' at some point in the preparation of Dr. Simpson's report. The crater, measured from crest to crest of the crater rim, was found to have a diameter of about 70 ft. Its depth we found to be only about $10\frac{1}{2}$ ft.

Our visit to the crater had been planned mainly for the purpose of searching for metallic spheroids similar to those we had discovered at the Arizona meteorite crater (fig. 2). Such vaporization droplets had been found only[1] at the large Arizona crater (4 000 ft. diameter) and the

[1] The spheres of metal enclosed in the impactite at Henbury and at Wabar are very much smaller (L. J. Spencer, Min. Mag. 1933, vol, 23, p. 387).

Odessa, Texas, meteorite crater (580 ft. diameter). They had not been found at the smaller Haviland, Kansas, crater (55 ft. by 36 ft.), nor, according to Russian reports, at the Sikhote-Alin craters, a group of craters in Eastern Siberia ranging up to 80 ft. in diameter. Since metallic spheroids are a condensation product of an exploded meteorite, it had been surmised that a crater of intermediate size (225 ft.) might throw light on the problem of their production. Our hopes in this regard were quickly dimmed, however, since no crater under 90 ft. in diameter had ever exhibited evidence of formation by explosive vaporization of the impinging meteorite. The Dalgaranga crater, we found, proved no exception.

We had also hoped to find some meteorite fragments similar to those described by Simpson, but our new metal-detector completely failed to function and we were forced to spend our time in a visual search for specimens and a magnetic search for spheroids.

There was a notable scarcity of meteorite specimens, and in two days the three of us recovered only 23 small irons with an aggregate weight of 149 g. A considerable quantity of magnetic particles was gathered to be processed after our return home. We puzzled over this paucity of meteoritic material. No piece larger than about 30 g. was recovered. We considered the possibility that perhaps the mass of the meteorite remained intact in the crater pit. However, the crater in all its visible aspects appeared to be an explosion crater produced probably not by vaporization but by a very violent fragmentation of the impacting mass. Yet, if that were true, why were there so few fragments? From what we could learn, only a few pounds of material had been found by the early visitors, and a more reasonable assessment of all reports would estimate the amount as merely a few ounces. We considered the possibility of a stony meteorite being responsible for the crater—perhaps one with a few lumps of metal scattered through it—but attempts to find any remnants of such a mass failed completely.

We attempted to locate a magnetometer in order to investigate the possibility of a residual mass in the crater depths. We visited several petroleum exploration companies, but neither they nor the university were able to supply such technical assistance. It was decided, therefore, to proceed to other objectives of our trip and further seek for an answer to the Dalgaranga puzzle after processing the materials collected. All of the other known Australian meteorite craters (fifteen in three locations) were on our itinerary; thus it was several months before we returned home to examine our Dalgaranga material.

When finally one of the little specimens was polished we found to our amazement that it was not a medium octahedrite, nor even a siderite. It was a mesosiderite (fig. 3), with a structure resembling that of Steinbach, the unique siderophyre. More of the specimens were cut, and while some were like the first others were true siderites; but none was a

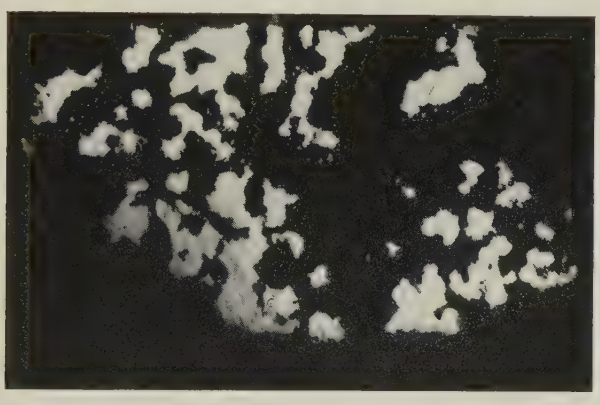

FIG. 3. Polished section of a small mesosiderite found near the Dalgaranga crater (×4).

simple medium octahedrite. They were brecciated, mostly showing a fine instead of medium octahedral pattern, and each fragment consisted of several areas showing differing alignments of their plates (fig. 4).

It was abundantly evident that we had depended too much on the Simpson report and that we had missed a great opportunity to gather important new information on meteorite crater problems. It was promptly decided that the authors should return to Australia for a more complete investigation.

We suspected that the paucity of meteorite fragments and the total lack of any but very small specimens might have been due to the larger masses having buried themselves and having thus escaped our surface search. We therefore took with us two detectors that had been adequately tested in the field. We planned to extend our surface search and to excavate to some extent within the crater. The Museum of Western Australia endorsed our plan, and we arrived at Dalgaranga on 18 October, setting up camp on the south-west rim of the crater.

Our first efforts were toward determining the true dimensions of the crater. A meteorite crater is a pit with an uptilted lip which is surmounted by a more or less prominent ridge of debris or rubble. This

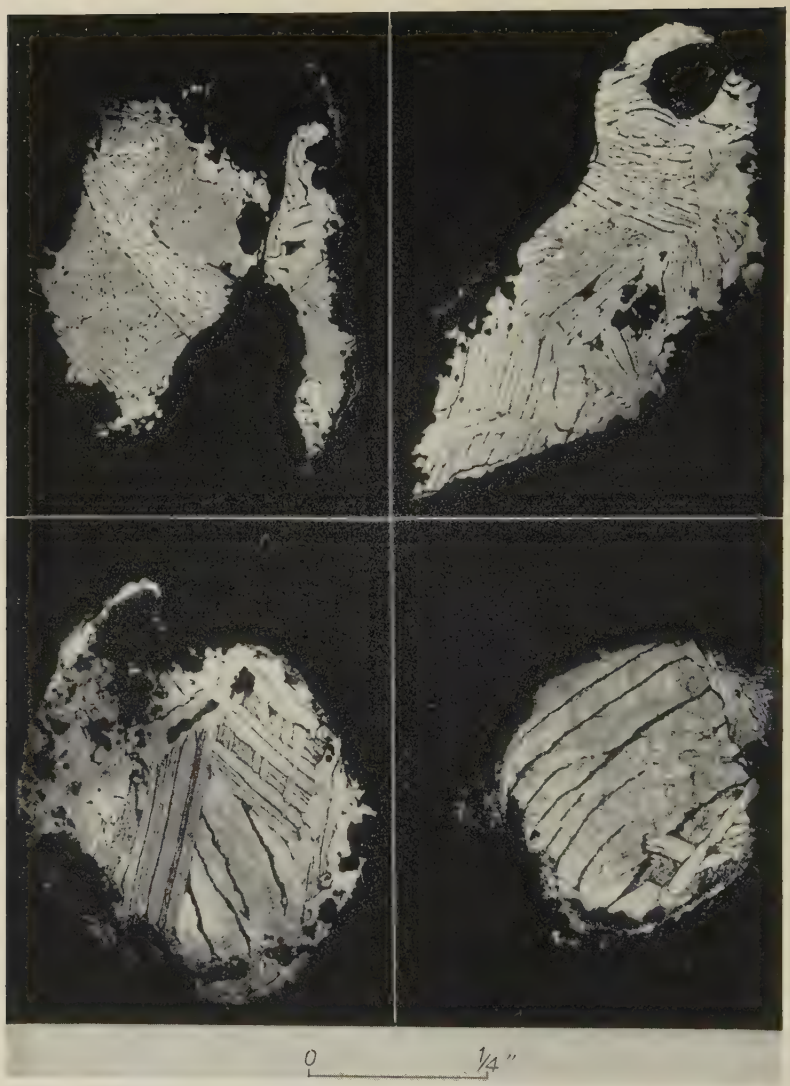


FIG. 4. Dalgaranga irons, showing some of the observed variations in structure.

ridge is generally spoken of as the rim, and is flattened and smoothed with age. It is always difficult, particularly in the case of old craters, to determine the exact crest of this rim in measuring the diameter of a crater. It is much more precise and meaningful to measure the pit from lip to lip.

On our first visit we had made only a rough crest-to-crest measurement; but on the second visit we made more complete measurements as follows:

*Diameters*

East–west, lip to lip, 69 ft. 11¼ in.; north–south, lip to lip, 70 ft. 4 in.; East–west, crest to crest, 86 ft. 1½ in.; north–south, crest to crest, 81 ft. 3½ in.

*Depths*

Measured from a cord drawn taut across the centre of the crater, crest to crest, between lowest points on the rim, 8 ft. 8 in.;

North-east–south-west between highest points on the rim, 12 ft. 9 in.; north–south crest to crest, 9 ft. 6 in.;

East–west crest to crest, 8 ft. 9½ in.; lip to lip, on various axes, 7 ft.–8 ft.

By carefully observing the crater lip we seemed to detect in it a bilateral symmetry. At a point 19° north of west there was an absence of rim rubble and the lip was tilted scarcely at all. Standing at this point one noticed that on either side the lip showed an increasing tilt or dip away from the pit; until, at points about 90° to either side, it stood at about 40° with the horizontal. From these points on around to a point opposite from where one stood the tilt of the lip diminished until it lay almost horizontal again. Inside the wall at this opposite point several large slabs lay as if they had been heaved up and then dropped back into the pit. The two greatest masses of out-thrown rubble corresponded to the most steeply tilted sectors of the lip, thus forming the two highest points on the rim.

The crater rim consisted of a mixture of large and small blocks with gravel, sand, and dust, some of which was as fine as flour. There was a peculiar difference in the character of the rim material on two sides of the pit. The south-western half of the rim was disintegrated granite, while the north-eastern half was largely laterite. The greatest mass of rim material lay in the north-east quadrant (fig. 5). Here large blocks of laterite, one measuring 97 in. by 46 in. by 20 in., were mingled with and predominated over those of granite. The next largest aggregate lay in the quadrant directly opposite and was all granite. These two types of rubble shared the other two quadrants. Inspection of the crater wall showed outcrops of laterite down to a depth of 40 in. in the north-east sector and none in the opposite wall.

Outside the crater rim the level plain consisted of quartz gravel from disintegrated granite sprinkled with irregular blocks of quartz up to 6 in. in diameter and irregular chunks of disintegrated granite. But on the north-west, north, and eastern sectors this material was mingled

Fig. 5. View looking north-east across the crater and showing the greatest aggregation of rubble, here mainly laterite.

with laterite rubble, and in much of the north-eastern portion was completely obscured by it. The massive jumble of large laterite blocks forming the north-eastern rim was very impressive. We could only conclude that before the impact there had existed a mound of laterite overlying the granite and that the meteorite struck the edge of this mound. Irregular blocks of laterite and granite of various sizes were scattered out to distances of 50 to 200 ft. from the crater rim, and an occasional

one was found even farther out. At two points on the west and south sectors there was an almost total absence of rim.

On the basis of our experience at other craters we felt justified in the belief that the majority of the meteorites were buried under a few inches of rubble or soil, and we first searched the inside walls and crater floor. Finding nothing, we made a few traverses over the plain immediately around and outside the crater rim. A few small irons were found, after which we set up four flagged stakes marking the cardinal points on the rim and four additional stakes at points 200 ft. from the former. We began a systematic coverage of the 200-ft. zone thus designated. The search only served to confirm our findings on the previous trip: that there existed a remarkable paucity of meteorite specimens.

Considering that, so far as we could learn, no search had ever been made aside from that by Mr. Willard, it seemed reasonable to suppose that whatever had been deposited at the time of the impact would for the most part still be present unless destroyed by weathering. Most of the pieces that we found were in a fair state of preservation, and we felt inclined to rule out the weathering factor. In 12 days of almost continuous searching by at least one instrument, and visual searching by one to three individuals, only 207 specimens with a combined weight of 1·1 kg. were recovered. Most of these weighed individually less than 5 g.; the largest weighed 57 g.

Laterite pebbles constituted a considerable nuisance throughout our investigation. They not only had almost the exact colour of meteorites, but a small percentage of them also caused a signal on the instrument which was indistinguishable from that produced by the little irons. However, in spite of this confusion, some of the areas most heavily infested with laterite were the areas most productive of meteorites.

Only the 200-ft. zone was covered systematically, but numerous areas of considerable size beyond the 200-ft. zone were also searched; in only one instance did these yield anything—three specimens were found beyond our 200-ft. flag on the north at 410 and 597 ft. from the crater. The map (fig. 6) shows the general distribution of finds. A few masses of oxide were found in the rim rubble on the north-east, east, south-west, and west sectors. One spot in particular was outstanding in this respect. At a point 52 ft. from our due north rim flag, 66 ft. from the due west rim flag, and 36 ft. from the nearest point on the north-west rim, we found under about 3–5 in. of finely pulverized rock seven small shale balls and a considerable quantity of oxide scale weighing altogether

484 g. This was all found within an area of less than 1 sq. yd. The spot is marked by an extra large symbol on our distribution map.

An experiment was carried out on an area of about 40 sq. yds. which had yielded a few small irons. It was raked with a garden rake to remove

Fig. 6. Distribution of meteorite finds at Dalgaranga. The dashed outlines indicate areas cleared of surface rocks before searching.

all rocks and pebbles that would prevent the most efficient use of the detector and then searched carefully, letting the detector coil down to within an inch of the soil surface. This search yielded 22 small fragments averaging about 1 g. each. The centre of this test area was 43 ft. from the due south-west rim. A similar area was tested in the same manner, where two small irons had been found on the surface, centring some 90 ft. from the rim 20° north of the due west radius. This test yielded nothing. A careful lookout for impactite was kept up at all times, but none was found.

During the second week we employed a digger in order to explore the depths of the pit. A trench was begun at the periphery of the crater fill, 18 ft. 9 in. from the centre stake, by stripping the fill from the wall and cutting a trench 3 ft. wide with its inner side cut vertically down until undisturbed rock was encountered. The trench was begun at a point

57° east of the due south radius and extended in an arc to a point 20° north of the due east radius. When we reached a depth of 18 in. we began to find, lying against and near the crater wall, small, heavy, rounded masses which registered on the detector. These occurred more frequently

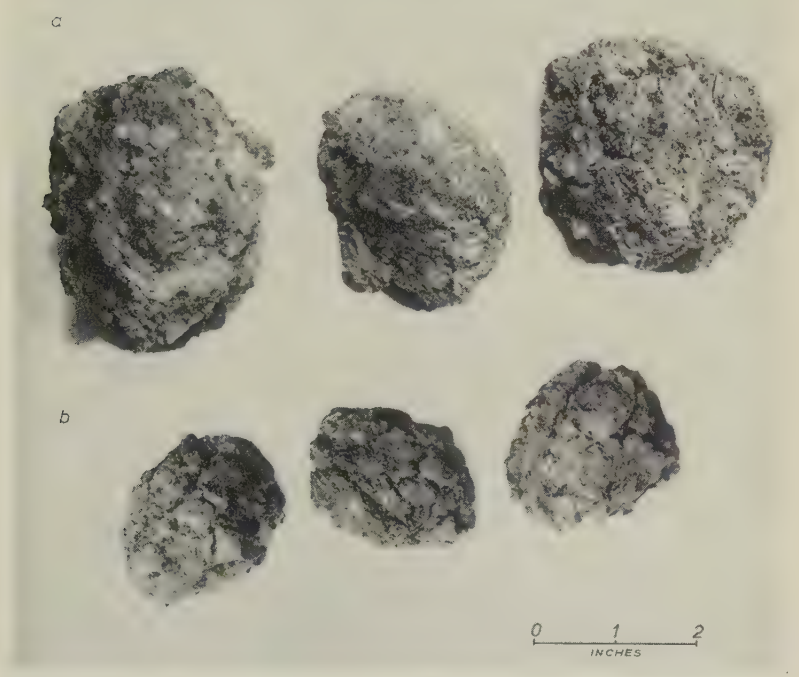


FIG. 7. Oxidized meteorite fragments from Dalgaranga crater, coated with disintegrated granite: *a*, mesosiderites; *b*, siderites, less abundant but more typical of other 'shale balls'.

as we went deeper. In this trench, the crater wall was encountered at a maximum depth of 12 ft. 7½ in. below the rim crest and the detector indicated that we should widen the trench inward toward the centre of the pit. We did so and found specimens in about the same abundance. In this widened trench we reached a depth of 13 ft. 3 in. below the rim crest and by this time had collected 280 specimens aggregating an estimated 20 lb. All specimens were small, the largest measuring about 3 in. in diameter (fig. 7*a*). They were of two kinds. The more abundant type looked like balls of disintegrated granite with a few rust stains, but

when broken one showed the familiar dark brown oxide. The other type was far less numerous and resembled the much fissured 'shale balls' of the Arizona crater (fig. 7*b*). The two kinds were intermingled. They sometimes occurred in clusters.

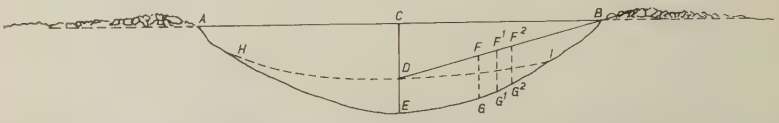


FIG. 8. Dalgaranga crater profile, north-east–south-west section. *ACB*, *DB*, stretched cords; *HDI*, present crater floor; *AEB*, original crater floor; $FG = 7$ ft., $F^1G^1 = 6\frac{1}{2}$ ft., $F^2G^2 = 6$ ft.

The deepest point reached was 15 ft., measured from a cord stretched from crest to crest over the central point of the pit. However, at this point the crest included some extra-high blocks of rim material. Measuring from lip to lip the depth was only 12 ft. 4 in. Projecting the same curve to the centre of the pit (fig. 8), we estimated that the central crater depth is 14 ft. 2 in. measured from the upturned lip, or about 13 ft. below the original plain. This estimate is of course based on the assumption of a bilaterally symmetrical crater, and our measurements were made on a radius at right angles to the longitudinal axis as we had determined it.

When our explorations had progressed to this point, we found that our digger had aggravated an old injury and was forced to quit work. The Yalgoo area, we learned, was even more destitute of diggers than the crater area was of meteorite fragments. Since we had insufficient time to import help from communities farther afield, we completed our detector-survey of the area that we had staked out and returned home.

*The meteorites.*

From the plain around the crater 207 specimens were recovered with a total weight of 1 098 g. A third of these averaged less than 3 g. each and the largest found weighed 57 g.; 118 specimens were cut and polished, and most of them etched: 64 were siderites, 25 were mesosiderites, 27 were a combination of siderite and mesosiderite, and 2 were aerolitic.

The siderites ranged in structu from the coarsest to the finest octahedrite, and in some specimens of only 1 or 2 g. two or more of these structures appeared. More than half of those etched, small as they were, proved to be made up of two or more units, each with its own orientation of the Widmanstätten structure (fig. 9).

Many of these irons showed deformation by pressure and some showed

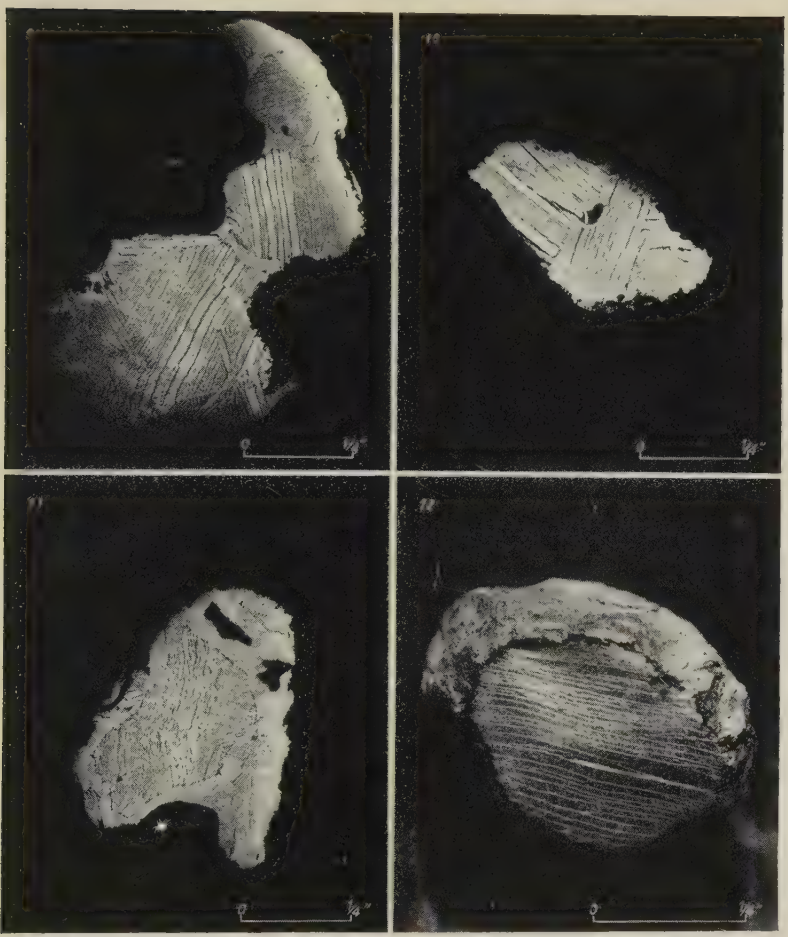

FIG. 9. Dalgaranga iron, 23-g. fragment; etched section showing differently oriented units, faulting, and displacements.

FIG. 10. Dalgaranga iron, 5-g. fragment; etched section showing faulting across 13 kamacite plates.

FIG. 11. Dalgaranga iron, 24-g. fragment; etched section showing area enveloped in swathing kamacite.

FIG. 12. Dalgaranga iron, 10-g. fragment; etched section showing parallel kamacite and taenite plates. Natural heating has eliminated Neumann lines but has not affected the taenite. The undeformed plates indicate that the oval shape is original, with the heat-alteration zone removed by weathering, or that irregularities have been lost by oxidation and scaling.

heat alteration sufficient to obliterate Neumann lines; a few showed diffusion of taenite; but others had not been altered by either heat or pressure. Several specimens were faulted, the kamacite and taenite plates showing displacements (figs. 9, 10). Some of the specimens showed only plessite in the sections polished, and others showed no plessite whatever. The prominence of taenite varied greatly from specimen to specimen. In several instances swathing kamacite enclosed normally-crystallized areas, and in a few formed dividing walls between differently oriented areas (figs. 10, 11).

Some specimens showed evidence of sufficient heating to have eliminated Neumann lines in the kamacite but showed no deformation of the plates nor any alteration of the taenite. One such specimen showed perfect lamellar arrangement of plates but betrayed no evidence of the Widmanstätten pattern (fig. 12). Areas of comparable size and structure are not unknown in normal octahedrites from other falls, but always appear as a part of the Widmanstätten lattice.

The material recovered from the excavation in the pit bore no resemblance to that we had found on the surrounding plains. It consisted of greyish-brown lumps, scarcely distinguishable from the rubble in which they were found except by their greater weight. These meteorite fragments were completely covered by adhering grains of disintegrated granite but a little rubbing removed this and the rusty brown mass of oxide which appeared resembled the concretions of many sandstone formations so familiar to all geologists (fig. 7).

We selected 41 representative specimens and began sectioning them on a diamond saw. The interiors thus revealed gave us quite a surprise. We were familiar with the various stages in the terrestrialization of meteorites, having sectioned hundreds of specimens from the Haviland crater and many from the Arizona crater, a few from the various Australian craters, the Odessa, Texas, crater, and the Wabar craters, besides many old weathered aerolites from the western plains of America that were unrelated to craters. But here was something different from all of them.

Since we had examined a number of the little specimens from around the crater, we naturally expected those from the pit to be of the same type. The cut sections looked more like the old weathered aerolites we had studied from the plains of Kansas and Texas than any previous crater specimens which we had seen; the cut surface was dark brown in colour, with numerous bright metallic-looking grains such as one finds in many old weathered chondritic aerolites.

As previously noted the specimens taken outside the crater were

mostly of the siderite variety, a few were mesosiderite, and two seemed to be unusual aerolites. As we proceeded with the examination we found that a few of the crater specimens showed a sideritic structure but the majority were completely unfamiliar to us.

We began polishing these strange specimens, whereupon their true

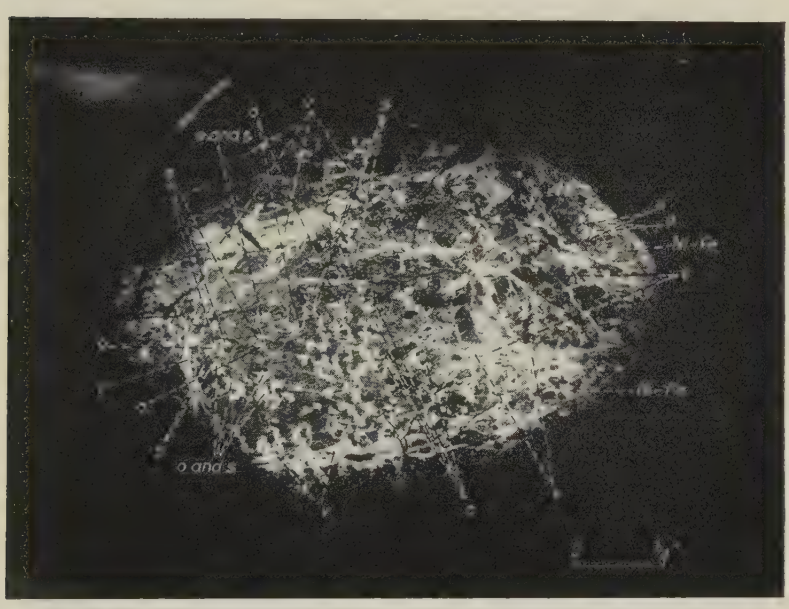


FIG. 13. Dalgaranga mesosiderite. Polished section showing metallic nickel-iron (Ni–Fe), oxidized nickel-iron (*O*), oxidized nickel-iron veins (*V*), and troilite (*S*).

character was revealed. What had appeared to us as a uniformly dark brown substance now presented a rather complex pattern. In fact, there were two patterns, both mesosiderite. Some presented the normal mesosiderite pattern that one sees in such meteorites as Mincy and Hainholz, except that the metallic ingredients of those well-known specimens were, in the Dalgaranga specimens, replaced by oxide pseudomorphs. Others had a very special structure resembling that of the unique siderophyre from Steinbach, Bavaria. The oxidized metallic constituents were set in a matrix of dark brown, somewhat granular, silicates (probably enstatite and olivine) in which were embedded microscopic grains of sulphide (fig. 13).

What had appeared to be metallic grains in the unpolished cut sections were now seen to be bright brassy sulphide (troilite). Angular and

irregular in shape, they lay embedded in the stony matrix or adjacent to and sometimes surrounding the metallic oxides. Upon subjecting several specimens to X-ray diffraction tests, Dr. Eugene R. Du Fresne of the University of Chicago identified the silicate mineral as 'rhombic pyroxene, probably bronzite', and the oxides as magnetite and goethite.

Traversing the above patterns was a network of oxide veins of the same colour and texture as the metallic oxide grains. These veins varied in width from 3 mm. to mere microscopic threads. They were adjudged to be also the product of weathering and appeared no different from the system of veins so often observed in all kinds of old weathered meteorites.

A few small remnants of taenite remained in the metallic state, having escaped oxidation; and, in rare instances, the thin taenite bands were sufficient to outline a Widmanstätten structure showing that a small sideritic body had been embedded in mesosideritic surroundings. This condition seems to present an explanation of the source of the small irons found on the outside of the crater and will be discussed presently.

There were also areas of stony matter that were devoid of any metallic oxide grains or bands. Some of these were of considerable size (fig. 15), and one naturally wonders if this sort of structure may have predominated in the original meteorite but was eliminated on impact.

Some of the stony matter presents a chondritic appearance but nothing has been seen that exactly corresponds to any of the chondrules with which we are familiar. The crater specimens are more or less encased in an arkosic zone consisting of granitic particles bound together by the metallic oxides from the enclosed meteorite fragments. In some cases this material had intruded itself into fissures and in at least one specimen a vein of granitic material traverses the entire specimen (fig. 15). Numerous small inclusions appeared to be graphite. One such was analysed by Dr. Du Fresne as a mixture of magnetite and graphite.

As previously mentioned there were a few specimens among those taken from our excavation that were of the siderite class (fig. 7*b*). These, after the removal of the loosely adhering grains of disintegrated granite, resembled the well-known 'shale balls' from the craters in Arizona, Texas, Australia, and Arabia. They were deeply fissured and bore polygonal exfoliation scales or blocks which had evidently remained in place simply because of the pressure of the terrestrial materials in which they were embedded.

When cut and polished they showed plainly the Widmanstätten structure; but all was in the form of oxides save for minute remnants of metal, mostly taenite, and these remnants were actually less prominent

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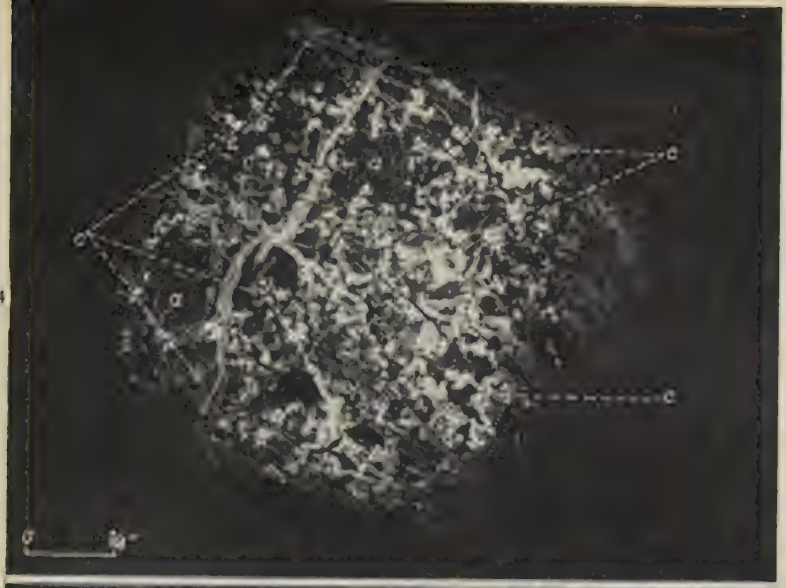


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Fig. 14. Dalgaranga oxidized mesosiderite from crater. Polished section showing areas of siderite (*s*) and aerolite (*a*), and inclusions of graphite magnetite (*c*). Some taenite remains unoxidized. The white areas are mainly oxidized nickel-iron. Numerous troilite grains are present but indistinguishable from oxides in the photograph.

Fig. 15. Dalgaranga oxidized mesosiderite from crater. Polished section showing metallic nickel-iron (Ni–Fe), graphitic matter (*c*), and laterite filling a fissure. Dark areas are stony matter, light areas oxide. Sulphide grains are distinguishable in the specimen but not in the photograph.

than in some of the mesosiderite type. On closer examination there also appeared inclusions of sulphide, quite unlike the sulphide of the mesosiderite specimens. Instead of the bright brassy colour, these were very dark, in some cases so dark as to be almost indistinguishable from the surrounding oxide except that they lacked the Widmanstätten structure

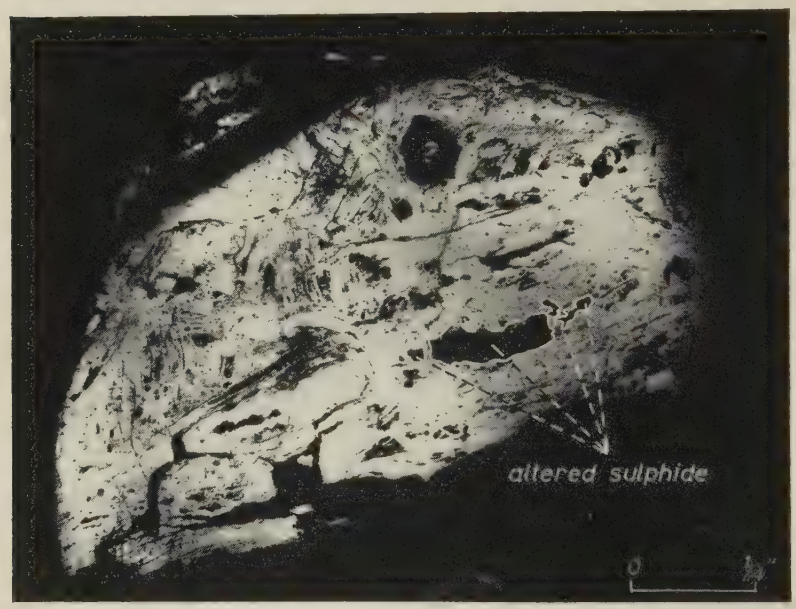


FIG. 16. Dalgaranga oxidized siderite. Polished section showing traces of Widmanstätten pattern. Dark areas are cavities and fissures, except for the altered sulphide indicated and the rusty porous remnant (?) which may also have been sulphide.

and differed very markedly in form. Instead of appearing as angular grains they were usually elongate, with ends and corners rounded, and were also much larger and in some instances showed a platy structure. The poor state of preservation suggests that this sulphide was of a somewhat different composition from that in the mesosiderite specimens. (Dr. Du Fresne has identified this sulphide as marcasite.) Nininger has called attention to the differences in meteoritic sulphides in several former writings.[1] Here we seem to have a great difference in susceptibility to the forces of weathering between the sulphides embedded in two phases of the same meteorite (fig. 16).

[1] Journ. Geol., Chicago, 1929, vol. 37, no. 50; Out of the Sky (Dover Publ. Inc., New York), 1959, p. 116.

The meteorite specimens from within the crater showed the same wide range in their Widmanstätten structure as prevailed among the plains specimens, and they also were composed of several areas of differing orientation.

*Discussion.*

Certainly the Dalgaranga crater presents more unusual features than any other of the known meteorite craters. It seems evident that here we have a crater formed by a meteorite that was not wholly metallic, and yet one that must have carried within it a greater variety of metallic constituents than have ever been found associated with any other crater. Naturally one feels obliged to attempt to depict the kind of meteorite that struck here.

In working with the material gathered from the plain around the Dalgaranga crater we were repeatedly reminded of the Estherville, Iowa, mesosiderite which fell in 1879 and from which many small siderite pellets were recovered. That great fall was witnessed, and in addition to the little pellets which were collected, several sizable masses were recovered, the largest of which weighed 431 lb. By studying sections of the large masses a good understanding of the original meteorite was obtained. It consisted of a stony mass in which were embedded many small nodules of metal as well as aggregates of metallic grains which frequently anastomosed to form more or less of a reticulum.

The Estherville meteorite was seen to disintegrate in the stratosphere. It left a long dust column, and the little 'iron pellets' were scattered along the last 7 miles of its course, at the end of which was buried the 431-lb. mass. This mass did not form a crater but came to rest in a hole some 14 ft. deep in marshy land. The mass had been so effectively checked in its flight by air resistance that it did not disintegrate on impact. Apparently its terminal velocity was just short of that necessary to produce disintegration, for it did shed some small pieces, which were picked up near the hole, and a few fragments were found in the hole during the excavation. Had the Estherville meteorite been of sufficient magnitude for a mass of larger size to survive to reach the ground at a higher velocity, one can conceive of a result comparable to what must have happened at Dalgaranga.

In making the comparison, however, there are certain important differences besides that of size that must not be overlooked: We found no justification at Dalgaranga for believing that any fragments survived comparable in size to the several large masses at Estherville. The profile

of the Dalgaranga crater was comparatively flat, indicating a meteorite of low tenacity: whereas in the case of Estherville, which we know was also a meteorite of low tenacity, a considerable mass survived to form a deep narrow hole. Nearly all of the recovered Estherville material, aside from the few large masses, was in the form of small nickel-iron pellets, the majority of which were found 1 7 miles back along its trail; whereas the Dalgaranga metallic pellets were found within 200 ft. of its crater. The bulk of the recovered Estherville mesosiderite was found, intact, within its deep pit: the bulk of the Dalgaranga mesosiderite was found within a wide shallow pit and in the form of many small pieces. And considering the size of the crater, an exceedingly small amount of meteoritic matter was recoverable at Dalgaranga.

In view of all known facts we conclude that at Dalgaranga a large mass, composed principally of stone but containing nests of mesosideritic and sideritic materials, struck the earth at sufficient speed to disintegrate on impact. The stony constituents were reduced to dust and have been scattered and carried away by the forces of erosion. Such mesosiderite and siderite fragments as survived the blast and were thrown out of the pit have, with rare exceptions, succumbed to the same forces. Those that were buried under the rubble have fared a little better. They have largely remained intact but have suffered many of the alterations that are inherent in the process of weathering.

In comparing Dalgaranga to Estherville we are not thinking quantitatively. We assume that the former was many times larger than the latter. Estherville is cited merely as a suggestion of the structural type of meteorite with which we are dealing at Dalgaranga. Neither do we believe that the two were of the same composition quantitatively. Dalgaranga is considered to have been a far more siliceous, or stony, mass. Had its metal-stone ratio been the same as that of Estherville (about 1:1) we believe there would have been several hundred or perhaps thousands of pounds of metallic fragments scattered about the crater. A crater 70 ft. in diameter would hardly be produced by a meteorite of less than several tons unless it came in at a very high speed, and all of our investigations at Dalgaranga point to a low speed at impact. We found no evidence of vaporization, no fused country rock or silica-glass (impactite), and we saw no evidence of great heat in association with the specimens excavated from the pit.

We believe, therefore, that a mass of 10 to 20 tons, composed of perhaps 90 % silicates, sulphide, and carbon, struck the ground at minimum speed. Being composed mainly of brittle constituents it was thoroughly

shattered, producing a shallow crater and a huge dust cloud along with a shower of fragments. Because of their predominantly stony character, most of the fragments have been reduced to dust by attrition, but nodules of metal set free by the blast have survived with more or less loss in the form of oxide scale.

In the crater, buried under rubble, fragments were shielded from attrition but were victims of oxidation and corrosion. These, although their compositions and to some extent their structures have been altered, still furnish us with clues to the nature of the parent meteorite.

It would be of considerable satisfaction to know the age of this crater. Simpson's report stated that it was formed before 1910, a statement probably based on the ranch manager's judgement of the age of the largest mulga tree that he saw growing in it. But a tree from which we cut a branch with 54 annual growth rings had germinated on $5\frac{1}{2}$ ft. of fill that had been accumulated in a semi-desert climate similar to that prevailing at the Arizona crater.

At the Arizona crater buildings erected on the floor of the crater before 1905 registered no measurable accumulation of sand and dust in the year 1950. There appeared to have been no noticeable accumulation of sediments around the 54-year-old tree after its germination in the Dalgaranga crater. It is generally agreed by geologists that the age of the Arizona crater is of the order of 50 000 years. The conditions observed in the wall, rim, and floor of Dalgaranga indicate a somewhat younger crater. From the data available we conclude that the fill in the Arizona crater pit has a maximum depth of about 800 ft., which is 66 % of the total pit depth as measured from the level of the surrounding plain. In Dalgaranga the fill has reached a depth of 5 ft. 6 in. which is 40 % of the pit depth.

The arkosic rock of Dalgaranga probably succumbs more readily to the forces of erosion than do the limestones and sandstones in Arizona. Drilling reports in the Arizona crater indicate that most if not all of the meteoritic material buried therein is in the form of oxides, a condition much the same as we found at Dalgaranga. If our hypothetical description of the Dalgaranga meteorite is correct, then it should have been less tenacious than the metallic mass that struck in Arizona. It seems a fair estimate that the Australian fall occurred 25 000 years ago, more or less. We did collect some small amounts of charcoal from several points in the rim and a very small amount in the crater pit. These have not been analysed. They may have some useful information but one cannot know whether they were buried at the time of the impact or subsequently.

# *Silicate melts with indications of ino structures.*

By E. Christiaan de Wys, M.A., Ph.D.

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[Communicated by the Editor; read 31 March 1960.]

*Summary.* Evidence is presented for the existence of silicon-oxygen chains up to 1 000 Å. in length in melts of $CaMgSi_2O_6$ and of $LiAlSi_2O_6$ at temperatures a little above the melting point.

THE structure of silicate melts has pressing importance to geochemists, mineralogists, ceramicists, and slag metallurgists. Since ino-silicate compounds such as $CaMgSi_2O_6$ (diopside) and $LiAlSi_2O_6$ (spodumene) have petrological as well as industrial significance the synthetic melts of these compounds were chosen for this study.

Goldstein and Davies[1] in their work on phosphate linear polymers pointed out that the conflict between views concerning the presence and orientation of chain like structures in supercooled melts suggests the value of additional evidence for or against the existence of chain 'molecules' in glasses.

*Preparation of the bulk samples.* Pure $CaCO_3$, MgO, $Al_2O_3$, $SiO_2$, and $Li_2CO_3$ were used to prepare a homogeneous glass for each composition corresponding to either $CaMgSi_2O_6$ or $LiAlSi_2O_6$. Each mixture was thoroughly fused in platinum containers until free of gas bubbles, after which the glass was analysed for correct chemical composition. Each glass was then thoroughly devitrified. The polycrystalline aggregates were then examined by optical microscopy, and X-ray and electron diffraction in order to ascertain whether indeed the particular compound with its particular ino structure had been formed.

The polycrystalline material was then remelted and cooled into a glass. This bulk glass was then carefully examined for absence of crystalline matter by means of a polarizing microscope (using objectives with NA up to 1·4), electron transmission with a resolution between 10 and 15 Å., and X-ray and electron diffraction. All these techniques indicated absence of crystalline material.

[1] M. Goldstein and T. H. Davies, Journ. Amer. Ceram. Soc., 1955, vol. 38, p. 223.

*Experimental methods and results.* The experimental glasses were examined in the bulk and fibre forms by means of high resolution petrographic microscopy, X-ray diffraction (von Laue type flat-back camera), and electron transmission (RCA EMU-2D electron microscope with double objective pole piece). The electron micrographs were selected on the basis of being in good focus and free of any astigmatism or image motion.

Diopside, an ino-silicate, was rapidly melted up to a temperature of 1 510° C. The supercooled bulk melt was examined for absence of crystalline material as described above. Numerous electron transmission photographs of this substance showed poorly oriented chain-like structures. The chains appeared to have lengths from 500 Å. down. An attempt was then made to ascertain whether longer linear elements could be formed in the diopside melt. Since the chains are preformed in the crystalline state where their maximum length theoretically would be the length of the crystal in the direction of its *c*-axis (to which they are parallel) and in general their minimum length the length of the *c*-axis for the unit cell, it was felt that pyrolytically grown crystals held just below the liquidus for 96 hours might furnish longer chains.

Since it appears that the devitrification rate of a one-component melt would be related among other factors to the size of the nuclei present, it was interesting to note that any attempt to pull glass fibres from the diopside melt prepared from larger crystals failed even at 1 510° C. owing to very rapid crystallization. A similar melt prepared from smaller crystalline material allowed glass fibres to be pulled at 1 393° C., or only about 2° C. above the liquidus.

Spodumene, also an ino-silicate, was examined in the bulk glass form by means of high resolution electron transmission. Linear elements were clearly visible in the photographs. The chain length ranged again from 500 Å. down. Attempts, similar to those employed on the diopside melt, to enlarge the Si–O chains resulted in chains approximately 1 000 Å. long (fig. 1).

It seemed reasonable to assume that if indeed Si–O types of chains are present in the melt it should be possible to orientate such units by mechanically pulling glass fibres at high speeds from such fluids. From an electrically heated platinum container with a small funnel in the bottom glass fibres with diameter ranging from $16 \times 10^{-5}$ to $21 \times 10^{-5}$ in. were pulled by means of a high-speed electrically driven spindle. These fibres were then examined by powder electron diffraction techniques and were found to be free of crystallites.

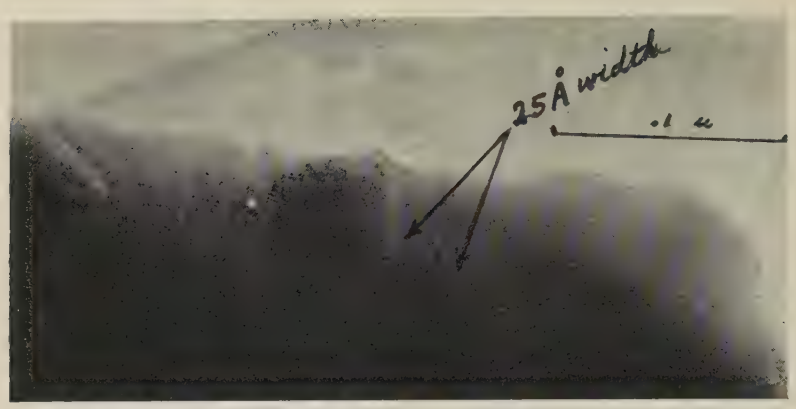
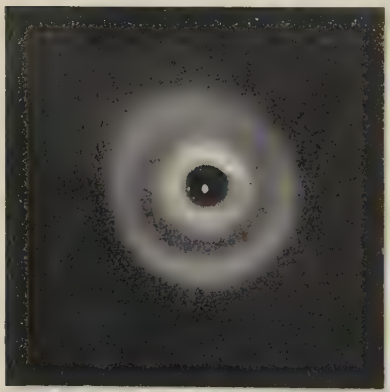
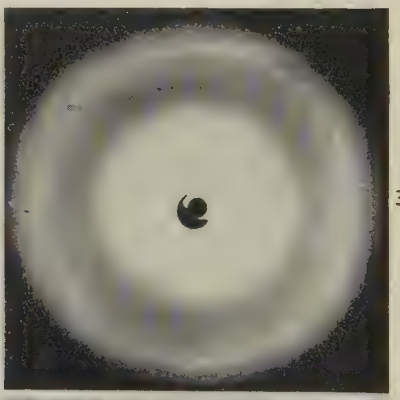
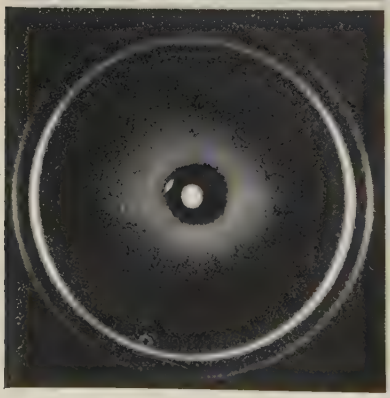
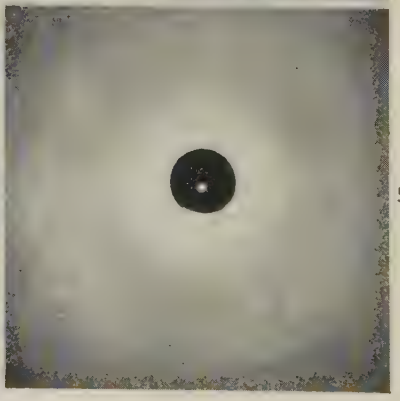



FIG. 1. Electron transmission picture of an $LiAlSi_2O_6$ glass fibre.




FIGS. 2–4. X-ray diffraction patterns of $LiAlSi_2O_6$ glass fibres.
FIG. 5. X-ray diffraction pattern of a commercial high-silica glass fibre.

The classical method of determining preferred orientation of polymers in fibres is by the use of von Laue type flat-back cameras. Such a unit employing copper radiation was employed. Figs. 2 to 4 show some of the typical results obtained. It appears that pulling rates and temperature strongly affect the results obtained. We are in the process of determining the effect of some of these variables on the degree of orientation. Examination of the patterns obtained indicated that diffraction is occurring from (*hk*0) planes at right angles to the long axis of the chains. Apparently groups of chains have locally aligned themselves so well as to form regions of order resulting in a few very mosaic *hk*0 reflecting units. For comparison purposes an X-ray pattern of normal commercial (high silica) glass is included, fig. 5. Optical examination of the fibres revealed a slight anisotropism resulting from different optical densities parallel and at right angles to the long axis of the fibres.

*Conclusions.* The author has attempted using some of the modern tools and techniques available to discover whether indications concerning the structure of some specific one-component silicate melt could be obtained. The experimental data so far assembled and the theoretical discussions brought forth in a previous paper appear to indicate to us that some hesitancy in the acceptance of the general network theory of silicate glasses might well be defensible. The author is well aware that considerable work remains to be done and in a later paper will publish some additional data on other specific one- and two-component silicate melts.

# *A thermodynamic analysis of the system anorthite–åkermanite.*

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[Communicated by the Editor; taken as read 2 June 1960.]

*Summary.* From thermodynamic considerations of the system anorthite–åkermanite it appears that the melts in this system are ionic in nature. The liquidus relation in this system would thus seem to afford confirmation of the theory, based on conductivity measurements, that silicate melts such as molten anorthite dissociate into such ions as $Ca^{2+}$ and $(Al_2Si_2O_8)^{2-}$.

Further thermodynamic calculations involving no unreasonable assumption lead to a close reproduction of the experimental liquidus curve of åkermanite. This lends added strength to the belief in the stable existence of åkermanite down to the eutectic; no evidence in support of the claim that åkermanite becomes unstable below 1 325° C. (Osborn and Schairer, 1941) was encountered.

According to Osborn *et al.* (1954) the presence of substantial $Ca^{2+}$ increases the desulphurizing potential of blast furnace slag. The thermodynamic treatment of the binary system anorthite–åkermanite leads to the conclusion that both phases dissociate in the molten state and in mutual solution to yield $Ca^{2+}$; it therefore appears probable that a high concentration of these minerals in the slag would have a salutary effect on the slag chemistry.

THE system anorthite–åkermanite is a binary system located in the petrologically and technologically significant four component system $CaO$–$MgO$–$Al_2O_3$–$SiO_2$. Experimentally this system has already been investigated (de Wys and Foster, 1956) as has the ternary system anorthite–åkermanite–diopside of which it is a join (de Wys and Foster, 1958). The location of these systems in the basic four-oxide system is indicated in fig. 1. This figure indicates the position of the ternary system in the tetrahedron; a hollow, transparent tetrahedron has been used to permit a clearer view of the plane under consideration.

Technologically, some of the industrial glasses, cements, and virtually all usual iron blast-furnace slags are included in the lime–magnesia-alumina–silica system, according to McCaffery *et al.* (1927), Koch (1933), Osborn *et al.* (1954), and Prince (1951). Since apparently the properties of slag are not mere composites of the properties of $SiO_2$, $Al_2O_3$, $MgO$,

and CaO, but rather of the mineral compounds present, an investigation of the interrelationships of some of the minerals should be useful. According to Martin and Derge (1943) a knowledge of possible liquid

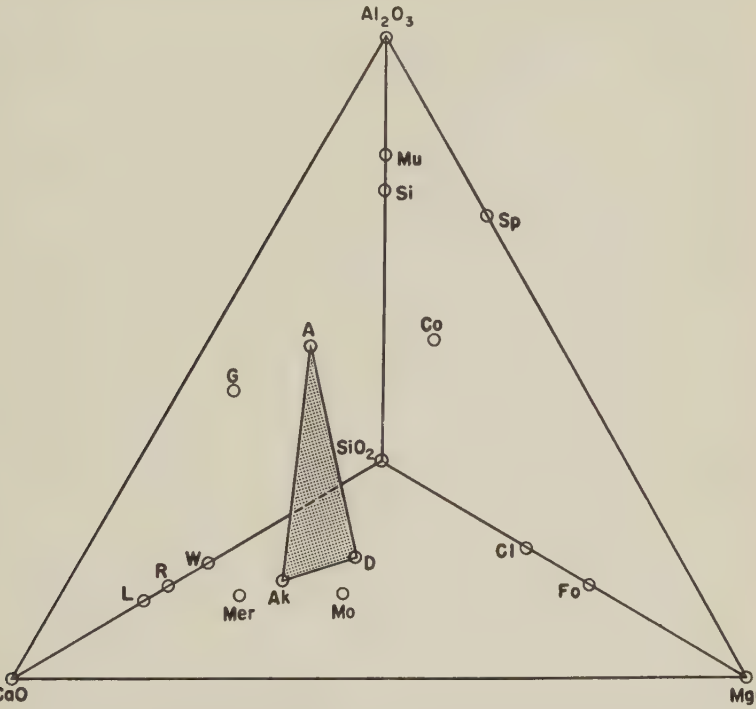


FIG. 1. The lime–magnesia–alumina–silica tetrahedron. The shaded area represents the anorthite–åkermanite–diopside ternary plane. The abbreviations have the following significance: A, anorthite; D, diopside; Ak, åkermanite; Mu, mullite; Si, sillimanite; Sp, spinel; Co, cordierite; G, gehlenite; L, larnite; R, rankinite; W, wollastonite; Mer, merwinite; Mo, monticellite; Fo, forsterite; Cl, clinoenstatite.

structural units in the slag would greatly clarify the nature of the chemical reactions in such a fluid, and would help to explain reactions between mineralogical melts and metal. Such knowledge would facilitate a greater control of slag chemistry. Accordingly, a thermodynamic analysis of the system anorthite–åkermanite was undertaken in an attempt to formulate possible structural units present in silicate melts of this type.

*Thermodynamic discussion and results.* Experimentally it has been established that the freezing-point depression of a melt depends both on the

nature of the solvent and on the degree of dissociation or association of the solute. Assuming an ideal solution, an equation relating these two factors to each other follows directly from the Clausius-Clapeyron equation. The equation may be expressed as follows: $\Delta T_f = RT_0T/\Delta H_f i \ln N_1$ where $\Delta T_f$ is the freezing-point depression of the solution, $T_0$ is the melting-point of the primary phase, $T$ is the liquidus temperature of the primary phase region, $\Delta H_f$ is the latent heat of fusion of this phase, $R$ is the gas constant in calories per mole, $N_1$ is the mole fraction of the solvent. $i$ is the so called van't Hoff factor which may be defined as the ratio of the effect produced by a mole fraction of an electrolyte to the effect observed for an equal mole fraction of non-electrolyte. If $i = 1$, the solution is non-electrolytic.

By and large, a two-component system may be considered practically ideal if the molecular volumes of the components are nearly equal (Wagner, 1952). Therefore, since the molecular volumes of anorthite and åkermanite are about 100·6 and 93·3 respectively, assuming the density of anorthite as 2·765 (Morey, 1954) and of åkermanite 2·922 (Ervin and Osborn, 1949), it would appear that such a system may be considered ideal compared for example to a system involving either of the above phases with diopside, which has a molecular volume of about 66·3.

The above equation was therefore utilized for the calculation of a theoretical diagram for the system anorthite–åkermanite with a view to comparing experimental and calculated liquidus curves. Since the $\Delta H_f$ ranges of values for anorthite and åkermanite have been published (Goranson, 1942) and the $T_0$ for these compounds are well known it is possible to calculate $\Delta T_f$ ranges for any selected value of the mole fraction of either component acting as a solvent and for various $i$ factors.

Fig. 2 shows two calculated liquidus zones. The upper zone is the result calculated with an $i$ factor of 1, while the lower zone shows the result of a calculation with an $i$ factor of 2. Since the lower calculated zone shows an excellent correlation with the experimental curve, it is reasonable to conclude that an $i$ factor of 2 is more applicable to this system. The $i$ factor of 2 may be taken as a strong indication that the silicate melt is electrolytic in nature. Such a conclusion appears to be quite conservative in that it agrees with numerous authors such as Doelter (1907 and 1908), Farup *et al.* (1924), Martin and Derge (1943), Bockris *et al.* (1948), and Barth and Rosenquist (1949). All of the above observed that the numerous silicate melts with which they were concerned did act as strong electrolytes.

The foregoing treatment permits the construction of a tentative model of the anorthite–åkermanite silicate melt. Darken and Gurry (1953), Bockris *et al.* (1948), Barth and Rosenquist (1949), and others, believe that the essential difference between solid and molten silicate lies in the

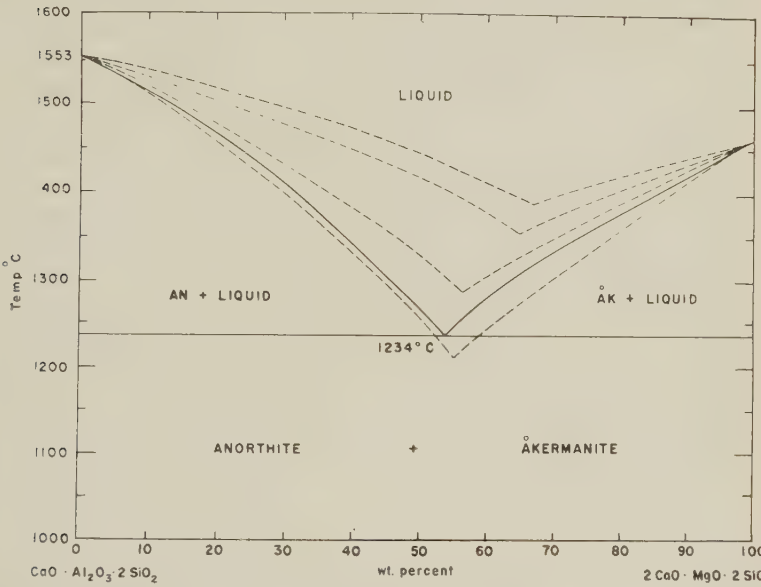


FIG. 2. Comparison of theoretical and experimental liquidus curves for the system anorthite–akermanite. Upper zone lying between the dashed lines is the calculated liquidus zone on the basis of a $\Delta H_f$ value for anorthite ranging from 375 to 505 J/g. and a $\Delta H_f$ value for åkermanite between 315 and 445 J/g., and an $i$ factor of 1. The lower liquidus zone, lying between the lower pair of dashed lines represents the results of freezing point lowering calculations with similar $\Delta H_f$ values and an $i$ factor of 2. Note that the experimental curve (solid line) falls within the lower liquidus zone.

degree of order or disorder. According to this point of view the liquid state is characterized by an extended network lacking symmetry and periodicity. Bockris *et al.* consider the molten silicates as consisting of irregularly arranged silicate rings and chains with cations in the interstices. Martin and Derge in experimenting with liquids of anorthite compositions indicate that at 1 450° C. calcium migrated to the cathode while a complex alumina silicate moved to the anode. They concluded, therefore, that in the molten slag such a composition is present as $Ca^{++}$ and a complex silico-aluminate ion. Blau (1951) indicated that in

super-cooled silicate melts there are two distinct types of oxygen ions. He divided them into those that bridge two 'network-forming' cations, and those that are connected to only one 'network-forming' cation and have valence charges balanced by the considerably more loosely held and distant 'network-modifying' cations. Blau then apparently indicates that when the ratio 'network-forming' cations to oxygen is 1:2 all the oxygens in the silicate melt are bridging. This agrees with tables by Evans (1952) concerning similar ratios in silicate structures. Blau proceeds to provide further ratios and their connexion to the types of oxygen present. A melt of anorthite has definitely a ratio of 1:2 and thus such a liquid would tend to have all bridging oxygens. A complex $(Al_2Si_2O_8)^{--}$ as well as $Ca^{++}$ would therefore result from such an ionic melt. Such a point of view would then agree with the observations by Martin and Derge. Also, such dissociation of the dissolved anorthite into ions of that type would explain an $i$ factor of 2 for the åkermanite liquidus curve. In general the åkermanite composition would tend to classify it among the sorosilicates. Eitel (1952) prefers to classify åkermanite among the phyllosilicates; he indicates that the $Si_2O_7$ groups are combined with $(MgO_4)$ tetrahedra to form fivefold annular structures, complexes of the composition $(Mg_2Si_4O_{14})^{8-}$. The $i$ factor of åkermanite electrolyte would then be $2\frac{1}{2}$. Considering Blau's calculation and looking upon Mg as a network former from his point of view, the ratio would be 0·428. This would allow such a composition to fall into the category of 3 to 4 bridging oxygens per tetrahedron of $(SiO_4)$ or $(MgO_4)$. According to Evans such a ratio would be classified as a sheet structure.

The fact that an $i$ factor of 2 appears to fit the experimental curve while structural considerations tend to indicate a factor of $2\frac{1}{2}$ might be due to incomplete dissociation of the units.

*References.*

Barth (T. F. W.) and Rosenquist (T.), 1949. Amer. Journ. Sci., vol. 247, p. 316.
Blau (H.), 1951. Trans. Soc. Glass Techn., 35, p. 304.
Bockris (J. O. H.), Kitchener (J. A.), Ignatowicz (S.), and Tomlinson (J. W.), 1948. Discuss. Faraday Soc. vol. 4, p. 265.
Darken (L.) and Gurry (R.), 1953. Physical Chemistry of Metals. McGraw-Hill Book Co., New York.
de Wys (E. C.) and Foster (W. R.), 1956. Journ. Amer. Ceram. Soc., vol. 39, p. 372.
—— —— 1958. Min. Mag., vol. 31, p. 736.
Doelter (C.), 1907. Monats. Chem., vol. 28, p. 1313.
—— 1908. Ibid., vol. 29, p. 607.

EITEL (W.), 1954. The Physical Chemistry of the Silicates. Univ. Chicago Press, p. 47.

ERVIN (G.) and OSBORN (A. F.), 1949. Amer. Min., vol. 34, p. 717.

EVANS (R. C.), 1952. An Introduction to Crystal Chemistry. Univ. Press, Cambridge, p. 241.

FARUP (F.), FLEISCHER (W.), and HOLTAN (F.), 1924. Chim. et Ind., vol. 12, p. 11.

GORANSON (R. W.), 1942. Geol. Soc. Amer., Special Paper 36.

KOCH (L.), 1933. Neues Jahrb. Min., Beil.-Bd. 67, Abt. A, p. 401.

MARTIN (A. E.) and DERGE (G.), 1943. Trans. Amer. Inst. Mining Met. Eng., vol. 154, p. 104.

MCCAFFERY (R. S.), OESTERLE (J. R.), and SCHAPIRO (L.), 1927. Amer. Inst. Mining Met. Eng., Techn. Publ. no. 19, p. 1.

OSBORN (E. F.), de VRIES (R. C.), GEE (K. H.), and KRANER (H. H.), 1954. Journ. Metals, vol. 6, p. 33.

OSBORN (E. F.) and SCHAIRER (J. F.), 1941. Amer. Journ. Sci., vol. 239, p. 715.

PRINCE (A. T.), 1954. Journ. Amer. Ceram. Soc., vol. 37, p. 402.

PRUTTON (C. F.) and MARON (S.), 1951. Fundamental Principles of Physical Chemistry. MacMillan Co., New York, p. 193.

WAGNER (C.), 1952. Thermodynamics of Alloys. Addison-Wesley Press Inc., Cambridge, Massachusetts.

# *On a skarn monazite occurrence from the Namib desert near Usakos, South-West Africa.*

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[Read 3 November 1960.]

*Summary.* An unusual monazite deposit of metasomatic origin is described. The monazite occurs as randomly oriented crystals in a dolomitic marble. The chemical composition and optical data of the monazite are given.

DURING 1959, in the course of a geological investigation in the Karibib–Swakopmund area of South-West Africa, a unique monazite deposit was examined at a locality some 21 miles west-south-west of the town of Usakos. The monazite occurs as large, randomly oriented, reddish-brown, platy crystals or aggregates up to 5 in. in length, embedded in a coarse, iron-stained dolomitic marble. This remarkable rock has been exposed in a number of prospectors' pits that lie approximately 4 miles north 15° west of the Ebony railway stop on the Usakos–Swakopmund line. At this locality large pebbles of residual monazite are seen scattered over a considerable area in the desert.

## *Geological environment.*

The general geological configuration of this sector of South-West Africa has been described by Gevers (1934 *a*, *b*, and *c*). In the main, the area consists of high-grade regionally metamorphosed sediments of the Damara 'System' folded along regional axes trending east-north-east, and characterized by synkinematic granites and post-orogenic quartz veins, together with uranium, lithium-beryllium, copper–zinc, and tin–tungsten pegmatites. One of the most important structural marker-horizons within the Damara 'System' is the Marble Series (Gevers, 1934*a*, pp. 313–319) consisting of up to 3 000 feet of marble with interbedded biotite-schist, para-amphibolite, amphibolitic biotite-schist, and, in the basal portions of the series, thin quartzite horizons. Typical bedded grey metamorphosed limestones of this series crop out near the monazite locality described in this communication, but the intervening ground is covered with superficial deposits.

*Petrography.*

The brown dolomitic host rock (excluding the monazite) consists of about 90 % of dolomite, 5 % of calcite, and 5 % of the following accessories: magnetite, graphite, and pseudomorphs after earlier skarn silicates. The dolomite grains are mostly rounded and embayed, and are from 1 to 3 mm. in diameter. The calcite forms irregular grains, which are partly interstitial, and is also observed in small veinlets often associated with the larger monazite crystals. The accessory minerals, including the smaller monazite grains, are typical of many minerals found in skarn deposits in that they exhibit rounded, corroded margins. Dominant amongst the accessory constituents are pseudomorphs after possible original skarn silicates. Individually these now consist of rosettes of a serpentine-like mineral and secondary carbonates enclosed within a framework of goethite. Magnetite is found in small distorted crystals, which are mostly fresh and highly magnetic. Graphite is common and consists of small, rounded flakes. The monazite found in the marble varies in size from minute rounded grains to hand-size, platy crystals weighing up to some 2 kg. The smaller crystals are golden yellow in colour, whilst the larger ones are reddish brown owing to inclusions of red iron oxide along the cleavage planes. In general appearance, the monazite closely resembles certain varieties of chalybite. For the most part, however, the monazite is free from intergrown inclusions and secondary alteration products. Some crystals, nevertheless, do contain inclusions of calcite, dolomite, and the other accessories, suggesting a rather late period of formation of the monazite.

*Geochemical considerations.*

The rare-earth elements are normally concentrated in both the granitic and syenitic suites of rocks. Monazite, one of the most abundant rare-earth minerals, is a characteristic accessory in granitic rocks and is also found in large crystals and aggregates in pegmatites. Amongst alkaline rock associations, monazite has been recorded from many carbonatite complexes, particularly from African localities (Garson, 1959).

Although much work has been done on the distribution of rare-earths in the granitic (pegmatite) monazites, comparatively few analyses are available of monazites from alkaline complexes. Murata *et al.* (1957, 1959), and Heinrich *et al.* (1958), have found that in pegmatitic monazites the sum of the atomic percentages of the more basic rare-earth elements La, Ce, and Pr, with respect to total rare-earth elements, varies between

some 50 % and 80 %. In monazites from alkaline environments, however, this quantity appears to exceed 80 %. Moreover, in pegmatitic monazites the distribution of the three dominant rare-earth elements is generally: Ce > La > Nd or Ce > Nd > La. In contrast, in monazites from alkaline rocks the tendency seems to be Ce > La > Nd with the percentage of La approaching that of Ce. Another significant feature regarding monazites from these two suites lies in the thoria content. Granitic monazites are always thorium-bearing and their thoria content varies from some 3 to 18 wt. %. In contrast, in monazites from carbonatites the thoria appears to be low and is generally well below 1 %.

TABLE I. Chemical analysis and optical data of monazite from the Namib desert. Analyst: O. von Knorring.

| | | | |
|---|---|---|---|
| $SiO_2$ | 0·13 | Sp. gr. | 5·15 (Berman balance) |
| $ThO_2$ | 0·70 | $\alpha$ | 1·787 ±0·002 |
| $Ce_2O_3$ | 33·65 | $\beta$ | 1·789 ±0·002 |
| $La_2O_3$* | 23·0 | $\gamma$ | 1·842 ±0·002 |
| $Nd_2O_3$* | 10·0 | $2V_\gamma$ | 14°±1° |
| $R_2O_3$† | 2·18 | | |
| $P_2O_5$ | 30·10 | | |
| | 99·76 | | |

* Semi-quantitative spectrographic determinations by Miss J. M. Rooke.
† Approx. amount of other rare-earths by difference.

The chemical analysis of the Namib Desert monazite is given in table I. In addition, spectrographic determinations have shown traces of Na, Mg, Al, Ca, Mn, Y, Zr, Pr, and Pb; Sm, Eu, Dy, Ho, and Yb were not detected. The high values of Ce and La, and the low thoria, are typical features of monazites associated with carbonatites as outlined above. It is interesting to note that this monazite, developed in a carbonate rock, should show the same chemical characteristics. The close areal association of the monazite occurrence with other bedded skarns (wollastonite, diopside, sphene, &c.) suggests that the distinctive dark-brown marble host rock is part of the metasedimentary Marble Series of the Damara 'System' that has acted as a reservoir for migrating liquors bearing rare-earths and phosphorus and related to the regional phase of pegmatite emplacement. This suggested mechanism of fixation of monazite is comparable with that envisaged by Gevers (1929) to explain the presence of cassiterite in the coarse-grained meta-limestones of the Marble Series at Arandis some 18 miles to the west-south-west. Although other rare-earth minerals are known from many skarn deposits,

monazite has rarely been observed in large amounts. Heinrich (1958, p. 249) records monazite-bearing carbonate layers in schists and gneisses from Lemhi County in Idaho. The carbonate rock there consists of calcite with locally associated typical skarn assemblages of actinolite, baryte, chalybite, pyrite, magnetite, ilmenorutile, garnet, zoisite, apatite, and monazite. Microscopically the thorium-low monazite appears as subhedral to euhedral crystals replacing calcite and actinolite, and was apparently one of the latest minerals to crystallize.

There is no doubt about the economic potentialities of the present occurrence, and detailed investigation may reveal other deposits connected with the Marble Series of this area.

*References.*

Garson (M. S.), 1959. Rept. No. MSG/38, Geol. Survey of Nyasaland.
Gevers (T. W.), 1929. Trans. Geol. Soc. South Africa, vol. 32, p. 165.
—— 1934*a*. Neues Jahrb. Min., Beil.-Bd. 72, Abt. B., p. 283.
—— *b*. Ibid., p. 399.
—— *c*. Ibid., Beil.-Bd. 73, Abt. B., p. 27.
Heinrich (E. Wm.), 1958. Mineralogy and Geology of Radioactive Raw Materials. McGraw-Hill Book Company, Inc., New York.
—— Borup (R. A.), and Levinson (A. A.), 1958. Bull. Geol. Soc. America, vol. 69, p. 1580.
Murata (K. J.), Rose (H. J., Jr.), Carron (M. K.), and Glass (J. J.), 1957. Geochimica Acta, vol. 11, p. 141.
—— Dutra (C. V.), Teixeira da Costa (M.), and Branco (J. J. R.), 1959. Ibid., vol. 16, p. 1.

# *Ages of uraninite from two British localities.*

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*Summary.* Uraninite from Geevor Mine, Cornwall, has been analysed by the complete lead method and an age of 290±7 million years has been accepted. Similar studies of uranium from Tyndrum Mine, Perthshire, give an age of 230±8 million years. The significance of the results is briefly considered.

THIS is the first of a series of short papers to be published in this Journal presenting age determinations on uranium and thorium minerals. The work is co-ordinated by the Atomic Energy Division of the Geological Survey of Great Britain (hereafter abbreviated A.E.D.). Chemical analyses and lead separations are undertaken by the National Chemical Laboratory (N.C.L.) and isotopic analyses by the Atomic Energy Research Establishment, Harwell (A.E.R.E.).

## *Uraninite from Geevor mine, Cornwall.*[1]

Uraninite at Geevor Mine, Pendeen, near St. Just, occurs in small amounts in the sulphide-rich parts of the lodes close to the margins of the central quartz leaders. The lodes are developed on the north-western

[1] A preliminary account of the determination was issued (1959), with a limited circulation, under the title Age Determination Report No. 6, Atomic Energy Division, Geological Survey of Great Britain. Since then tables (Stieff *et al.*, 1959) incorporating the latest decay constants have become available, and the results now quoted are read from them; this has increased the accepted age by the negligible amount of 2 m.y.

margin of the Land's End granite and generally trend in a north-west–south-east direction. Ore from which the uraninite was concentrated came from the north-western extensions of the tin-bearing lodes, below the ninth level.

Initial concentration was made by James tables at the mine and the material was further purified by superpanner and electromagnetic separator. The fraction of uraninite obtained was pure except for a small amount of cassiterite. This was allowed to remain as it was considered that any contribution of lead from this source would be negligible. The analytical results and apparent ages derived from them are given in table I.

TABLE I. Geevor uraninite.

| *Chem. anal. wt. %* | | | *Lead-isotope proportions in* | | | *Isotopic ages in m.y.* | |
|---|---|---|---|---|---|---|---|
| | | | *Uraninite.* | *Galena.** | *Uraninite corrected.* | | |
| | | $^{204}Pb$ | $0{\cdot}0026 \pm 0{\cdot}0002$ | 1 | — | 207/206 | $302 \pm 85$ |
| Pb | 3·05 | $^{206}Pb$ | $94{\cdot}2 \pm 0{\cdot}04$ | 18·32 | 94·15 | 206/238 | $290 \pm 7$ |
| U | $73{\cdot}60_8$ | $^{207}Pb$ | $4{\cdot}95 \pm 0{\cdot}04$ | 15·55 | 4·91 | 207/235 | $291 \pm 15$ |
| Th | $1{\cdot}80_2$ | $^{208}Pb$ | $0{\cdot}891 \pm 0{\cdot}014$ | 38·10 | 0·792 | 208/232 | $308 \pm 30$ |

* Analysis of galena specimen presented by Geevor Tin Mine Ltd.

The agreement between the apparent ages is satisfactory and it is thus concluded that the uraninite has suffered no significant loss or gain of uranium, thorium, or their decay products. The $^{206}Pb/^{238}U$ age of $290 \pm 7$ m.y.[1] can be given with a higher degree of accuracy than the others, and is therefore taken as the accepted age of the mineral. It is not implied that all uranium mineralization in the south-west of England is necessarily of the same age. This will not be known until the additional analyses now being undertaken have been studied.

The age of the Geevor lodes is not known precisely from stratigraphical evidence. They cut 'killas' which is most probably of Devonian age; and lodes associated with the Dartmoor Granite, 100 miles to the east, cut Carboniferous rocks of Namurian age. Holmes (1959) has adopted the view that granite emplacement and mineralization occurred during mid-Morganian time. Kulp *et al.* (1960), on the other hand, have suggested that the granites are probably of very late Stephanian or Permian age. At present there is insufficient evidence for a choice to be made between these opinions or to enable any acceptable alternative to be put forward.

[1] m.y. = million years.

It is of interest to consider the Geevor results in relation to the ages which have been obtained from analyses of biotites from the Dartmoor and Land's End granites (table II). The spread of the results from the latter is considerable, and it must be questioned whether the correct result has yet been obtained for this material. The most recently reported ages for Dartmoor biotite, namely K–A 290 m.y., Rb–Sr 285±8 m.y., are compatible with the accepted age of the Geevor uraninite.

TABLE II. Ages of Dartmoor and Land's End biotite, in m.y.

| | *Potassium–Argon* | | | *Rubidium–Strontium* |
|---|---|---|---|---|
| *Reported by:* | *Faul** | *Faul*† | *Kulp* et al. | *Lambert and Mills*‡ |
| Dartmoor ... ... | 295 | 290 | 271±5 | 285±8 |
| Land's End ... ... | 330 | — | 250±15 | 270±9 |

Analyses for each locality were made on material from the same biotite concentrate.

* These results (Faul, 1960) are recalculated from the original data given by Mayne *et al.* (1959). They were originally published as Dartmoor 305 m.y. and Land's End 340 m.y.

† This is a new determination (Faul, 1960).

‡ It is understood (R. St. J. Lambert, personal communication) that these results (Lambert and Mills, 1960) are preferred to those obtained earlier from the same samples and published by Kulp *et al.* (1960).

### *Uraninite from Tyndrum, Perthshire.*

At Tyndrum a quartz–galena–blende lode known as the Hard Vein traverses folded Moinian quartzites and quartz–mica schists. The vein strikes north-north-east–south-south-west nearly parallel to a major tear fault, but for most of its length is a few hundred yards to the west of the fault. At its south-western extremity the vein meets the fault plane at an acute angle, but does not appear to cross it. Sporadically distributed within the Hard Vein are very minor calcite–baryte–uraninite–chalcopyrite occurrences, which from the field evidence appear to be of later age (W. H. Clyne, unpublished report).

The uraninite analysed was taken from fresh dump material, together with a galena specimen typical of the material occurring in the main quartz–galena–blende vein. The uraninite (variety pitchblende) occurs as botryoidal clusters several centimetres in diameter set in a calcite matrix. Chalcopyrite is distributed as irregular blebs throughout the specimens examined, and is quite abundant within the uraninite. Small amounts of galena are present, unevenly and very finely disseminated within the uraninite and occasionally as larger inclusions in chalcopyrite. This galena does not occur in a sufficient quantity for a separate analysis

to be made. The uraninite was separated from the gangue and sulphides electromagnetically. The concentrate thereby obtained consisted of uraninite, which retained the very fine inclusions of chalcopyrite and galena, with a small amount of calcite adhering. The analytical results and the apparent ages derived from them are given in table III.

TABLE III. Tyndrum uraninite.

| *Chem. anal. wt. %* | | *Lead-isotope proportions in* | | | *Isotopic ages in m.y.* | |
|---|---|---|---|---|---|---|
| | | *Uraninite* | *Galena* | *Uraninite corrected* | | |
| Pb 6·95 | $^{204}$Pb | 0·95±0·02 | 0·0268 | (−0·007) | 207/206 | 247±470 |
| U $67{\cdot}37_5$ | $^{206}$Pb | 47·0±0·14 | 0·4751 | 30·04 | 206/238 | 230±8 |
| Th nil | $^{207}$Pb | 16·3±0·20 | 0·4138 | 1·53 | 207/235 | 232±50 |
| | $^{208}$Pb | 35·7±0·20 | 1·0 | — | | |

The lead-isotope analyses show that common lead amounts to 68 % of the lead present in the uraninite concentrate. It is therefore important to consider the isotopic composition of the lead used for making the common-lead correction. The common lead forming the Tyndrum main-vein galena has a model age of about 470 m.y., which is approximately twice the apparent age of the uraninite. Its composition is close to that given by Moorbath (1959) for galena from the Abergairn and Ballater area of Aberdeenshire. If the common-lead correction is made using a composition corresponding to 230 m.y., the lead/uranium ages, although not greatly altered, become more discordant, namely: 206/238, 229 m.y.; 207/235, 259 m.y. The 207/206 age, being very sensitive to discrepancies between the lead/uranium ages, becomes 546 m.y. Thus despite its greater model age, galena from the main vein at Tyndrum provides the more satisfactory common-lead correction. For greater accuracy the correction is based on the 208 rather than the 204 isotope, thorium being absent.

The age accepted for the uraninite is the $^{206}$Pb/$^{238}$U value of 230±8 m.y. This has the smallest analytical error, and as shown is not significantly altered by variations in the composition of the common lead. According to Holmes's (1959) revised geological time-scale, this is equivalent to an Upper Permian age. The significance of the difference in the 'ages' of the uraninite and galena will be considered in a future communication.

## *Appendix: Accuracy.*

The method of calculation is based on Tables for the Calculation of Lead Isotope Ages by Stieff, Stern, Oshiro, and Senftle (1959). The accuracy

given with each apparent age takes into account errors arising from analytical limitations and from the uncertainties in the accepted values of the physical constants, as given by Stieff *et al.* The errors have been obtained by substituting extreme values for each analytical result in the various equations so as to obtain the maximum and minimum ages. Where the largest variation from the mean exceeds 10 m.y., it is given to the nearest 5 m.y. above.

The accuracy of the chemical analyses, in terms of the quantity measured, is: $U_3O_8$ $\pm 0{\cdot}1$ % (for $U_3O_8 \geqslant 1$ %), $U_3O_8$ $\pm 1{\cdot}0$ % (for $U_3O_8 < 1$ %), $ThO_2$ $\pm 1{\cdot}0$ %, Pb $\pm 2{\cdot}0$ %. The errors quoted with the lead-isotope analyses are the standard deviations on ten measurements in each case.

Errors in the isotopic composition of the galena used for common lead correction have not been taken into account. In general the quantity involved is sufficiently small for any such errors to be negligible.

*References.*

Faul (H.), 1960. Bull. Geol. Soc. Amer., vol. 71, p. 637.

Holmes (A.), 1959. Trans. Edinburgh Geol. Soc., vol. 17, p. 183.

Kulp (J. L.), Long (L. E.), Giffin (C. E.), Mills (A. A.), Lambert (R. St. J.), Giletti (B. J.), and Webster (R. K.), 1960. Nature, vol. 185, p. 495.

Lambert (R. St. J.) and Mills (A. A.), 1960. Ann. New York Acad. Sci. (in press).

Mayne (K. I.), Lambert (R. St. J.), and York (D.), 1959. Nature, vol. 183, p. 212.

Moorbath (S.), 1959. Ibid., p. 595.

Stieff (L. R.), Stern (T. W.), Oshiro (S.), and Senftle (F. E.), 1959. U.S.G.S. Prof. Paper 334-A.

# *The cummingtonite problem.*

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[Read 3 November 1960.]

*Summary.* An examination of available chemical analyses shows that the anthophyllite and cummingtonite series of amphibole minerals are not isodimorphous. Whilst the anthophyllites are truly lime-free amphiboles, small amounts of calcium are essential to stabilize the monoclinic lattice of cummingtonites, which should be regarded as lime-poor amphiboles, analogous to the lime-poor pyroxenes. The existence of synthetic clino-anthophyllites is considered.

THE relationship between cummingtonite and anthophyllite has been a source of discussion since 1930, when Johansson made a comparative study of these minerals and tremolite. This work showed the similarity of the structures of the two monoclinic minerals, and the difference between these and the orthorhombic anthophyllite lattice.

An examination of the available chemical analyses (Layton, 1959) shows that although cummingtonite and anthophyllite can both be represented approximately by the formula $(Mg,Fe)_7Si_8O_{22}(OH)_2$, the most commonly occurring anthophyllites are magnesium-rich, whilst cummingtonites are usually iron-rich. For this reason, Winchell (1931) suggested that the magnesian composition is more stable as an orthorhombic structure, whilst the monoclinic form is more stable for iron-rich members. Sundius (1933) denied that the two minerals were isodimorphous and showed that anthophyllites contain 6–9 mol. % more alumina and ferric oxide than otherwise similar cummingtonites. This conclusion is also in general accord with Collins's (1942) results from Strathy. Winchell's further presentation of the case for isodimorphism in 1938 depends mainly on the accuracy of identification of supposedly high-iron anthophyllites. Rabbitt (1948) showed by inference that Winchell's examples were in fact probably cummingtonites and that the existence of high-iron anthophyllites is doubtful.

The rocks of the Orijarvi region were quoted by Eskola (1950) as examples of the occurrence of anthophyllite and cummingtonite of identical composition in the same rock. Eskola cited optical evidence

only as the basis of his identification, despite Rabbitt's (1948) demonstration that this can lead to serious errors. Eskola also compared the relationship between cummingtonite and anthophyllite with the dimorphism between enstatite and clino-enstatite.

It seems to us that the following three points have a significant bearing on the problem: aluminium is present in quantity in some anthophyllites but is rare in cummingtonites; although some of the minerals from Strathy described by Collins (1942) as cummingtonites are relatively high in alumina, no X-ray data are given and it is probable that these are in fact anthophyllites. It cannot be maintained that a high aluminium content alone causes the change from monoclinic to orthorhombic symmetry, in view of the existence of high-aluminium monoclinic forms such as tschermakite. Manganese and calcium are usually present in significant quantities in cummingtonite, but are generally virtually absent in anthophyllites.

Many authors have noted the presence of calcium and manganese in cummingtonite, but it does not seem to have been suggested that they should be regarded as essential constituents. The present writers suggest that the monoclinic symmetry of cummingtonite is caused by small amounts of calcium and manganese occupying the positions of eightfold co-ordination, which are more fully occupied by calcium in the calciferous amphiboles such as tremolite. The ionic radius of manganese (0·83 Å. for eight co-ordination, Green, 1959) is larger than those of magnesium and ferrous iron to such an extent that it may conceivably occupy positions similar to calcium (1·03 Å.). A similar calcium–manganese diadochy seems to exist in some other minerals—for example, the garnets. It is clearly impossible to decide the location of the calcium and manganese by examination of the chemical analyses, but support for the above suggestions may be forthcoming from detailed X-ray analysis (it should be emphasized that the only certain distinction between the cummingtonite and anthophyllite groups requires the use of X-rays).

It is interesting to note that Eskola's (1950) cummingtonite from Muuruvesi contains 3·96 % of alkalis. The equivalent anthophyllite contains a negligible quantity. This is a further confirmation that the two minerals do not have identical compositions as claimed by Eskola and are not isodimorphous. The substitution of alkalis in the cummingtonite structure presents no difficulties on the present hypothesis.

The orthorhombic structure allows a closer packing of the silicon–oxygen chains than the monoclinic structure (Whittaker, 1960), and in

magnesium-rich environments the small size of magnesium will undoubtedly favour the former symmetry. In addition, magnesium-rich environments are commonly relatively poor in calcium. Thus, a chain-chromite dunite quoted by Dunham *et al.* (1958) contains 30·8 % MgO and only 0·8 % CaO. This has been altered hydrothermally to a chain-chromite–anthophyllite rock containing 28·1 % MgO and 0·2 % CaO.

On average, the anthophyllite series may contain 0·5 % of lime and alkalis. Amounts greater than this in older analyses probably represent impurities. It seems quite possible, however, for very small amounts of calcium and sodium to enter the lattice without destroying the orthorhombic symmetry, and for the resultant strain to be taken up by localized distortion. It is also possible that these atoms may occupy the normally vacant 'A' position (Whittaker, 1960). Because of the small size of aluminium, a similar argument to that for magnesium applies to the aluminium-rich anthophyllites or gedrites.

The increase in ionic radius from magnesium to iron, coupled with the fact that more calcium and manganese are normally present in environments richer in iron, means that under these circumstances the difference in packing density between the orthorhombic and monoclinic structures is less marked and the presence of calcium or manganese ensures stability of the monoclinic form. Some confirmation of the suggested cummingtonite formulation is provided by Eskola (1950) who points out that cummingtonite, not anthophyllite, normally appears in paragenesis with hornblende. On the basis of the theory suggested here, anthophyllite would only form together with hornblende if the rock was deficient in calcium and manganese to such an extent that none was available for the formation of cummingtonite.

In an experimental investigation of the cummingtonite–anthophyllite series, F. R. Boyd (Geophysical Laboratory, 1954–55 Annual Report, p. 117) claimed to have synthesized both amphiboles from mixes free from manganese and lime. The synthesis was found to be easier in the more iron-rich batches and asbestiform anthophyllites were said to form in the range $Mg_{50}Fe_{50}$ to $Mg_{40}Fe_{60}$, although it is also stated that no amphibole richer in iron than $Mg_{50}Fe_{50}$ could be produced. In accordance with the above theory, the instability of iron rich compositions is to be expected in the absence of calcium. It is also important to note that the monoclinic forms were only obtained in the composition range $Mg_{85}Fe_{15}$ to $Mg_{70}Fe_{30}$ at temperatures above 800° C. and close to the apparent breakdown interval. We believe that these clino-amphiboles should be regarded as clino-anthophyllite and not cummingtonite, and that we

see here a close parallel to the relationships between enstatite and clino-enstatite. The synthesis of iron-rich clino-amphibole similar in composition to naturally occurring grunerite is only to be expected in the presence of calcium or manganese.

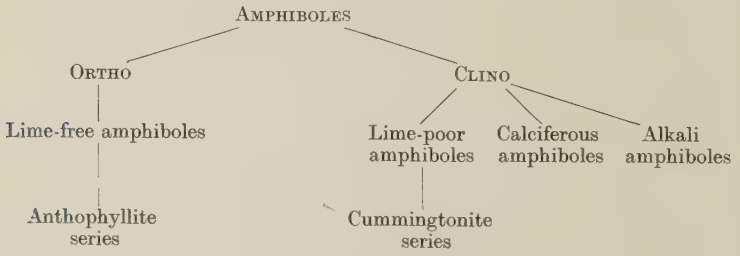
It is also possible to find naturally occurring examples of the persistence of monoclinic symmetry even in amphiboles rich in magnesium, if calcium and manganese are present. This is well shown by the analysis of a tirodite (Bilgrami, 1955).

It is of some interest to compare the cummingtonite–anthophyllite minerals with the pyroxene group. The calcic pyroxenes are monoclinic, as also are the high-temperature forms of the lime-free pyroxenes. There is an obvious analogy between the lime-poor pyroxene pigeonite and cummingtonite. So far as the writers are aware, there is no recorded instance of an ex-solution relationship between tremolite and anthophyllite due to instability of an original cummingtonite with falling temperature. It would seem, however, that this situation, analogous with the formation of diopside lamellae in orthopyroxene, is theoretically possible.

In conclusion it may be stated that whilst the formula

$$(Mg,Fe)_7Si_8O_{22}(OH)_2$$

may adequately represent the composition of the anthophyllite series, the suggestions given above, together with a detailed examination of available analyses (Layton, 1959), show that the formula for the cummingtonite series should be written as $(Ca,Mn)_x(Mg,Fe,Mn)_{7-x}Si_8O_{22}(OH)_2$ where $x$ is less than one. The major divisions of the amphibole series are then seen to be as in the diagram below:



*References.*

Bilgrami (S. A.), 1955. Min. Mag., vol. 30, p. 633.
Collins (R. S.), 1942. Ibid., vol. 26, p. 48.
Dunham (K. C.), Phillips (R.), Chalmers (R. A.), and Jones (D. A.), 1958. Overseas Geol. and Min. Resources Bull., Suppl. no. 3.
Eskola (P.), 1950. Amer. Min., vol. 35, p. 728 [M.A. **11**–330].
Green (J.), 1959. Bull. Geol. Soc. Amer., vol. 70, p. 1127 [M.A. **14**–408].
Johansson (K.), 1930. Zeits. Krist., vol. 73, p. 31 [M.A. **4**–356].
Layton (W.), 1959. Unpublished Ph.D. thesis, Durham.
Rabbitt (J. C.), 1948. Amer. Min., vol. 33, p. 263 [M.A. **10**–416].
Sundius (N.), 1933. Tschermaks Min. Petr. Mitt., vol. 43, p. 422 [M.A. **6**–64].
Whittaker (E. J. W.), 1960. Acta Cryst., vol. 13, p. 291.
Winchell (A. N.), 1931. Amer. Min., vol. 16, p. 250 [M.A. **5**–32].
—— 1938. Ibid., vol. 23, p. 329 [M.A. **7**–182].

## SHORT COMMUNICATIONS

### *A bismuth-bearing variety of bindheimite.*

In 1792 J. J. Bindheim[1] reported the results of his analysis of a 'Bleiocher' from Nerchinsk, Siberia, from which he concluded that it was a hydrated arsenate of lead. Since this time other workers have analysed similar minerals from the same locality, and concluded that they were dealing with an antimonate, not an arsenate, of lead. D. L. G. Karsten[2] gave the name Blei Niere to this mineral, but later it became known as bleinierite: Dana, however, thinking this name unsuitable, renamed it bindheimite.[3] Today bindheimite is a yellow earthy mineral composed of lead and antimonic oxides and water: it has the pyrochlore structure, and a variable composition.[4] With the exception of the discoverer (Bindheim) every investigator has found that antimony is present and has assumed it to be in the pentavalent state, although no evidence has been advanced in support of this.

An X-ray powder photograph of a 'bismuthic ochre' from Otjimboyo East, Karibib, South West Africa (B.M. 1929, 1843) showed it to be a well-crystallized fibrous bindheimite and a spectrographic examination indicated the presence, in addition to lead and antimony, of bismuth, iron, and calcium, together with very small amounts of aluminium, arsenic, sodium, and indium.

Chemical analysis gave the following results: $Bi_2O_3$ 9·7 %, PbO 41·1, $Sb_2O_5$ 30·0, CaO 1·0, $Fe_2O_3$ 3·0, $Na_2O$ 0·2, $As_2O_5$ 0·1, loss in weight on ignition (850° C.) 4·5 %, residue (insoluble in HBr and $HClO_4$) 8·0 % ($SiO_2$ 6·4 %), total 97·6 %. No tests were made to determine accurately the state of oxidation, although it was apparent that some of the elements were in their higher valency states since bromine was released on addition of hydrobromic acid. Had the mineral been decomposed completely by hydrobromic acid it would have been possible to determine the degree of oxidation of the mineral in the manner described below for bindheimite from Endellion. However, the mineral resisted attack by all reagents tried except hot concentrated sulphuric acid or a mixture of hydrobromic and perchloric acids, used in equal proportions, in which it dissolved on gentle warming. The antimony was determined, after reduction, by titration with standard potassium permanganate solution and the antimony was separated from the other metals either by distillation of antimony bromide at 160–180° C. from a solution of the

mineral in hydrobromic and perchloric acids,[5] or by treatment of the mixed sulphides with yellow ammonium sulphide. Bismuth and lead were estimated as oxybromide and chromate respectively. We are unable to account for the low summation but derive consolation from some other published analyses of bindheimite.[6]

To test further the method of analysis, a bindheimite from Endellion, Cornwall (B.M. 26757), was analysed and gave: PbO 43·0 %, $Bi_2O_3$ nil, $Sb_2O_5$ 43·7, FeO 2·3, $As_2O_5$ 0·5, residue 1·7, and loss of weight on heating (850° C.) 8·2 %; total 99·4 %. This mineral was easy to deal with, being readily soluble in cold hydrobromic acid in contrast to the related bismuth-bearing mineral just described. This fact made it a straightforward matter to ascertain the state of oxidation of the mineral and this was carried out in the following manner: the mineral (about 200 mg.) was transferred to a glass-stoppered flask followed by 1 g. potassium iodide dissolved in about 2 ml. of water; 5 ml. HBr were poured in and the flask swirled to hasten the dissolution of the mineral. When the mineral had dissolved, 5 ml. of chloroform were added to the flask and the liberated iodine titrated with decinormal sodium thiosulphate solution. If the liberated iodine is calculated in terms of $Sb_2O_5$, the result agrees with that obtained by direct titration of antimony with potassium permanganate, indicating that the iron was wholly in the ferrous condition, although, of course, the possibility exists that the mineral contains ferric iron and an equivalent amount of trivalent antimony. The Cornish bindheimite is just as indefinite in composition as are other specimens of this mineral; the atomic ratio of lead to antimony in the bismuth-bearing bindheimite, however, is close to unity.

The fibrous bindheimite has a cell dimension of $10{\cdot}4480 \pm 0{\cdot}0004$ Å. and is highly oriented with the [110] axis along the fibre. The Cornish bindheimite, on the other hand, is microcrystalline and the fibres unoriented, in which respect it conforms with other bindheimite specimens examined. The high degree of crystallinity in this fibrous bindheimite may be the reason for its resistance to chemical attack (cf. monimolite).[7] It would appear, therefore, having regard to the high degree of crystallinity and orientation, that this bismuth bearing bindheimite may be pseudomorphous after a fibrous bismuth-bearing lead antimony mineral such as kobellite.

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*References.*

[1] Schriften Ges. naturf. Freunde, Berlin, 1792, vol. 10, p. 368.
[2] Mineralogische Tabellen, Berlin, 1800, pp. 50, 77.
[3] System of Mineralogy, 5th edn, 1868, p. 591.
[4] B. Mason and C. J. Vitaliano, Min. Mag., 1955, vol. 30, p. 102.
[5] Some bismuth bromide also passed into the distillate.
[6] See, for example, E. V. Shannon, Econ. Geol. (Chicago), 1920, vol. 15, pp. 92, 93.
[7] B. Mason and C. J. Vitaliano, loc. cit.

## *Cahnite from Capo di Bove, Rome.*

CAHNITE, $Ca_2B(OH)_4AsO_4$, is the textbook example of a mineral crystallizing with point symmetry $\bar{4}$ and is thus better known than its rarity would suggest. The type locality is Franklin, New Jersey (Palache and Bauer, 1927), and the Klodeborg mine, Arendal, Norway (Bügge, 1952), is the only other recorded locality; cahnite is the last-formed mineral at both places.

A specimen labelled 'Gismondite, Capo di Bove, near Rome, Italy' was obtained by F. N. Ashcroft in 1906 from J. R. Gregory and Co. and later presented to the British Museum (Natural History) with the identity of the gismondine queried. My optical examination showed the refractive indices ($\omega$ 1·662) to be much too high for a zeolite, and that the mineral was probably cahnite; because the paragenesis is so unexpected, the identification has been confirmed by X-ray powder photograph and qualitative chemical analysis. The specimen, B.M. 1914, 339, a dark grey leucitic lava, has on one side part of a cavity lined with rounded aggregates of glassy phillipsite and a few white hemispheres of chabazite. Parts of the cavity, between the zeolites, are coated with a thin drusy layer of calcite on which are several dozen flattened sphenoids of cahnite. The crystals are clear and glassy, and of fairly uniform size (about $\frac{1}{3}$ mm.); the habit is dominated by slightly curved faces of $\{111\}$, the corners of the sphenoids being truncated by much smaller faces of $\{\bar{1}11\}$ (indices of Palache), and I have not seen any other form. None of the crystals examined was truly single, even when there were no external traces of another individual, but at the same time no true twin was observed goniometrically; between crossed nicols the extinction positions of the components differ by 1–2°. Despite careful searching, I have found no cahnite on other similar specimens in the Museum from Capo

TABLE I. X-ray powder data for cahnite from Franklin, New Jersey (B.M. 1918, 283). Camera diam. 114·6 mm., Cu·K$\alpha$ radiation. Cu-K$\alpha_2$ lines have been omitted.

| *d*, Å. | $I/I_0$ | *hkl* | $\sin^2\theta$ (*obs.*) | $\sin^2\theta$ (*calc.*) | *d*, Å. | $I/I_0$ | *hkl* | $\sin^2\theta$ (*obs.*) | $\sin^2\theta$ (*calc.*) |
|---|---|---|---|---|---|---|---|---|---|
| 5·02 | 20 | 110 | 0·0235 | 0·0236 | 1·108 | 7 | 424 | 0·4834 | 0·4834 |
| 4·67 | 20 | 101 | 0·0272 | 0·0273 | 1·090 | 1 | 541 | 0·4987 | 0·4987 |
| **3·56** | **100** | **200** | 0·0469 | 0·0472 | 1·055 | 1 | 622 | 0·5329 | 0·5333 |
| 3·10 | 2 | 002 | 0·0618 | 0·0620 | 1·043 | 1 | 631 | 0·5453 | 0·5458 |
| 2·833 | 19 | 211 | 0·0741 | 0·0745 | 1·035 | 1 | 514 | 0·5540 | 0·5541 |
| **2·640** | **48** | **112** | 0·0854 | 0·0856 | 1·015 | 1 | 613 | 0·5752 | 0·5754 |
| 2·514 | 15 | 220 | 0·0941 | 0·0944 | 1·011 | 2 | 116 | 0·5808 | 0·5809 |
| 2·336 | 17 | 202 | 0·1090 | 0·1092 | 0·9845 | 3 | 640 | 0·6120 | 0·6128 |
| 2·249 | 13 | 310 | 0·1175 | 0·1180 | 0·9748 | 2 | 444 | 0·6243 | 0·6248 |
| 2·215 | 15 | 301 | 0·1212 | 0·1218 | 0·9635 | 1 | 721 | 0·6391 | 0·6401 |
| 1·986 | 4 | 103 | 0·1508 | 0·1514 | 0·9548 | 9 | 712 | 0·6508 | 0·6512 |
| 1·951 | 5 | 222 | 0·1561 | 0·1565 | 0·9400 | 1 | 604 | 0·6714 | 0·6720 |
| 1·879 | 10 | 321 | 0·1684 | 0·1690 | 0·9369 | 3 | 316 | 0·6759 | 0·6752 |
| **1·818** | **52** | **312** | 0·1798 | 0·1801 | 0·9080 | 3 | 624 | 0·7196 | 0·7191 |
| 1·777 | 10 | 400 | 0·1882 | 0·1889 | 0·8993 | 1 | 651 | 0·7336 | 0·7344 |
| 1·733 | 3 | 213 | 0·1978 | 0·1986 | 0·8919 | 4 | 406 | 0·7458 | 0·7459 |
| 1·676 | 1 | 330 | 0·2116 | 0·2125 | 0·8870 | 1 | 800 | 0·7541 | 0·7542 |
| 1·660 | 5 | 411 | 0·2155 | 0·2162 | 0·8811 | 1 | 723 | 0·7642 | 0·7639 |
| 1·590 | 10 | 420 | 0·2354 | 0·2361 | 0·8777 | 1 | 107 | 0·7701 | 0·7704 |
| 1·558 | 2 | 303 | 0·2453 | 0·2458 | 0·8712 | 1 | 811, 741 | 0·7818 | 0·7815 |
| 1·540 | 2 | 402 | 0·2504 | 0·2509 | 0·8645 | 1 | 426 | 0·7939 | 0·7931 |
| — | 1 | 114 | — | 0·2717 | 0·8603 | 3 | 820 | 0·8016 | 0·8014 |
| 1·473 | 11 | 332 | 0·2738 | 0·2745 | 0·8488 | 1 | 615 | 0·8234 | 0·8231 |
| 1·427 | 3 | 323 | 0·2920 | 0·2930 | 0·8418 | 1 | 714 | 0·8372 | 0·8370 |
| 1·420 | 6 | 204 | 0·2950 | 0·2954 | 0·8363 | 1 | 660 | 0·8483 | 0·8485 |
| 1·412 | 3 | 422 | 0·2981 | 0·2981 | 0·8302 | 3 | 644 | 0·8609 | 0·8605 |
| 1·394 | 3 | 510 | 0·3061 | 0·3069 | 0·8284 | 6 | 307 | 0·8645 | 0·8647 |
| 1·386 | 3 | 501, 431 | 0·3099 | 0·3106 | 0·8253 | 1 | 545 | 0·8710 | 0·8702 |
| 1·318 | 8 | 224 | 0·3422 | 0·3426 | 0·8231 | 1 | 831 | 0·8756 | 0·8758 |
| 1·281 | 2 | 521 | 0·3570 | 0·3578 | 0·8094 | 2 | 813 | 0·9055 | 0·9054 |
| 1·272 | 11 | 512 | 0·3679 | 0·3690 | 0·8040 | 1 | 635 | 0·9179 | 0·9174 |
| 1·256 | 2 | 440 | 0·3763 | 0·3778 | 0·7980 | 1 | 734 | 0·9317 | 0·9312 |
| 1·219 | 2 | 530 | 0·3999 | 0·4014 | 0·7970 | 5 | 752 | 0·9341 | 0·9340 |
| 1·183 | 3 | 600 | 0·4239 | 0·4243 | 0·7932 | 4 | 840 | 0·9429 | 0·9428 |
| 1·166 | 4 | 404 | 0·4360 | 0·4363 | 0·7866 | 6 | 417 | 0·9589 | 0·9590 |
| 1·153 | 1 | 215 | 0·4460 | 0·4460 | 0·7836 | 1 | 910 | 0·9663 | 0·9664 |
| 1·148 | 1 | 611 | 0·4512 | 0·4515 | 0·7821 | 1 | 901 | 0·9698 | 0·9701 |
| 1·132 | 7 | 532 | 0·4625 | 0·4626 | 0·7771 | 1 | 606 | 0·9825 | 0·9816 |
| 1·122 | 6 | 620 | 0·4708 | 0·4714 | 0·7732 | 1 | 008 | 0·9922 | 0·9908 |

di Bove, from Vallerano, from Acquacetosa, or from Casale di Mostacciano; Mr. A. W. G. Kingsbury has examined Capo di Bove specimens in the Oxford University Museum, but without success. There seems little doubt of the locality, although details of the actual collecting are unknown, and the occurrence is the more interesting in the absence of other boron and arsenic minerals.

X X

X-ray examination shows that the powder pattern is identical with that of cahnite from Franklin, New Jersey, for which data are given in table I, and shows a very striking resemblance to that of xenotime, $YPO_4$. This resemblance suggests that the structure of cahnite is that of zircon (with which xenotime is isostructural), with Ca occupying Zr positions and alternating $B(OH)_4$ and $AsO_4$ tetrahedra in the $SiO_4$ positions. This arrangement results in a point symmetry of $\bar{4}2m$ unless the tetrahedral groups are slightly rotated about the $c$-axis from their positions in the zircon structure. A qualitative comparison of approximate structure factors calculated on this assumption with intensities obtained from the powder photograph shows that the suggested structure is reasonable. The space group is $I\bar{4}$, as determined from the observed point symmetry (Palache, 1941) and systematically absent reflections with $h+k+l$ odd. Cell dimensions derived by a modified Nelson–Riley extrapolation are $a = 7{\cdot}0952 \pm 0{\cdot}0015$, $c = 6{\cdot}1904 \pm 0{\cdot}003$ Å. Cell contents are thus $2[Ca_2B(OH)_4AsO_4]$, and the structure cell has twice the volume of the morphological cell (transformation: Palache and Bauer to new, $[1\bar{1}0/110/001]$). Adopting the new setting, cahnite and xenotime have comparable morphology when the difference in symmetry is taken into account, and both have a $\{100\}$ cleavage.

I wish to thank Mr. D. L. Williams for taking the photographs, Miss E. E. Fejer for measuring the films and calculating the results, and Dr. R. J. Davis for a method of obtaining cell dimensions using all the high-angle data.

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Bügge (J. A. W.), 1952. K. Norske Vidensk. Selskab. Förh., vol. 24 (for 1951), p. 79 [M.A. **12**–200].
Palache (C.) and Bauer (L. H.), 1927. Amer. Min., vol. 12, p. 149 [M.A. **3**–365].
Palache (C.), 1941. Amer. Min., vol. 26, p. 429 [M.A. **8**–226].

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*Note.* Results of an accurate structure determination of cahnite have now been reported at the Fifth International Congress of the International Union of Crystallography by C. T. Prewitt and M. J. Buerger, and my proposed structure is in substantial agreement with theirs. I have also been informed by Dr. C. M. Gramaccioli that building operations at Capo di Bove have made the quarries inaccessible for collecting.

## BOOK REVIEWS

BUERGER (MARTIN J.). *Vector Space and its application in crystal structure investigation.* New York (John Wiley and Sons) and London (Chapman and Hall), 1957. 347 pp. Price $12 or £4. 16*s*.

This book describes the application of the Patterson Function to X-ray crystal structure analysis.

The starting-point in crystal structure analysis is the set of experimentally determined intensities, $|F(hkl)|^2$, associated with the diffraction pattern of the crystal. The difficulty is that of determining the phases of the reflections. A. L. Patterson showed that the experimentally determined $|F(hkl)|^2$ used as coefficients in a Fourier synthesis give maxima that represent the lengths and orientations of the interatomic and intermolecular vectors *but not the positions of the atoms* in the crystal.

Although this is theoretically possible, the Patterson Function is difficult to interpret because maxima may represent the superposition of several vectors, and often Patterson maps display a uniformity of peak heights particularly if the crystal unit cell contains many atoms of about equal scattering power, for example carbon, nitrogen, and oxygen in organic compounds. In most cases where the Patterson Function has been successfully applied, the crystal contains atoms either of widely differing X-ray scattering power, or the atoms have some peculiar stereochemical configuration as in conjugated ring systems.

In spite of this difficulty of interpretation, the Patterson Function contains all the available diffraction information about the crystal. Since the war, there have been many attempts to put the direct interpretation of this function on to a quantitative basis. Having himself made significant contributions in this field, Professor Buerger shows authoritatively how this may be done in principle and practice. The Patterson Function is widely used in crystal structure analysis but is bewildering to a beginner; Professor Buerger is to be complimented on his attempt to treat it as a subject in itself.

The book may roughly be divided into two parts. The first nine chapters deal with the early use and the theory of the Patterson Function. Here Buerger has shown the relationship of Patterson symmetry to crystal symmetry and in these chapters one sees the experience of a good teacher taking the beginner over the many pitfalls of this subject. The next four chapters deal with image-seeking functions and superposition methods, which form the basis of the interpretation of Patterson

Functions. The book is well illustrated with examples of the determination of structures involving these techniques; quite a few have been worked out in Buerger's own laboratory, but as mentioned earlier all these examples depend for their solution either on the presence of heavy atoms or some known geometrical configuration of the components of the unit cell. There is a very useful list of references at the end of each chapter to published work in X-ray crystal structure determinations using these methods.

The book is singularly free of major errors. Nevertheless it has two main shortcomings. The first is that it is too bulky for a treatment of one particular aspect of crystal structure determination and the author could well have presented the same arguments in half the number of pages, thereby reducing the price of the book and so bringing it into the hands of more beginners, for whom he must have intended it. The second criticism is the author's failure to warn the beginner both of the limitation and of the difficulties of the interpretation of Patterson vector maps. A minor criticism is the insufficient mention of the increasing and important use of 'sharpened' Patterson Functions in the structure determination of complex compounds, as for instance vitamin $B_{12}$.

C. H. Carlisle

Burri (Conrad). *Petrochemische Berechnungsmethoden auf Äquivalenter Grundlage* (*Methoden von Paul Niggli*). Basel and Stuttgart (Birkhäuser Verlag), 1959, 334 pp., 66 text-figs. Price (bound) 38 Swiss fr.

The late Professor Paul Niggli introduced several methods for handling chemical analyses of rocks both to use them as a basis for classification and to calculate their actual or potential mineral composition. These methods are scattered through Niggli's many publications. The author here has collected them together and, by means of fully worked out examples, he explains the methods and illustrates their uses. No one is better qualified to do this than the author, who worked very closely with Niggli for many years at Zürich where he is Professor of Petrography.

An introduction reviews the various methods of graphical and diagrammatic presentation including triangular and tetrahedral diagrams. The first main chapter, 100 pages, deals with 'Niggli values' and their calculation from and to wt. %, cation %, and mol. (equivalent) %. The calculation of silica saturation (the 'quartz number'), norms and normative feldspars, and other values (*k*, *mg*, &c.) are explained. A projection of the *al-fm-c-alk* tetrahedra is used to depict eruptive fields,

and the system of 'magma-types' is explained and a full list of these is given.

The next chapter, 150 pages, deals with the 'Equivalent Norm' and the calculation of the 'Basis' components and the sequence in which they are to be calculated to arrive at the standard catanorm. The same three rock analyses as were used to illustrate the use of Niggli values are again used throughout this chapter.

The equivalent norm is perhaps the most useful of Professor Niggli's introductions to arithmetical petrography. The author here shows how variants of the standard catanorm can be readily calculated. This is particularly useful in the study of the metamorphic rocks by the calculation of the epinorm and mesonorms. Graphical methods of displaying the chemical and potential mineral compositions of analysed rocks using the Q-L-M and the Mg–Fe–Ca triangular diagrams are well illustrated by examples.

In a short, final chapter the author describes the calculation of wt. % of oxides to cation % as advocated and used by Barth and Eskola, and Barth's proposal for a standard 'cell' of 160 oxygens is discussed. The clearly printed tables at the end of the book enable both molecular and atom proportions for the principal rock-forming oxides to be read off rapidly, and another list gives the conventional formulae of the compounds used in the 'Basis' and 'Equivalent norm' calculations and of the equations which have been devised for their conversions.

W. C. S.

Brown (G. M.) and Nockolds (S. R.), managing editors. *Journal of Petrology.* Oxford University Press, 1960, vol. 1, no. 1.

This is a new journal, and the aim of the editors is to provide a place for the publication of original researches in the whole range of subjects which fall within a liberal definition of petrology. The subjects will include the physics and chemistry of rocks, their mineralogy and textures, and certain aspects of petrology involving the dating of rocks by natural radioactivity. Quantitative studies of rock-forming minerals, experimental physical chemistry relevant to petrology, and isotope geology will also be included, though regional studies will not be covered unless they lead to results fundamental to petrology as a science.

The journal is printed on a 10 by 7 in. page with a type area of 8 by 5 in. and is expected at first to run to 400-page volumes consisting of three numbers per year, published in February, June, and October.

The subscription price for three consecutive numbers is 80*s*. ($12) post free; single numbers 30*s*.

Smits (D. W.), editor. *World Directory of crystallographers and of other scientific officers employing crystallographic methods.* Utrecht (Published for the International Union of Crystallography by N. V. A. Ooshoek), 1960, 2nd edn., 134 pp. Price U.S. $1.50.

This second edition of the list first published in 1957 as Philips Laboratory Contribution No. 115 (edited by William Parrish), contains information on about sixty per cent. more persons and includes the complete membership of the American Crystallographic Association, which Association is not now issuing a separate membership list. Each entry gives the full name, date of birth, highest degree, appointment held with the address of the institution and telephone number, together with the chief crystallographic interest of the person concerned. The representation varies rather widely from country to country because the border-line has been differently drawn, as is shown by the numbers of persons included for U.S.A., 879, U.K., 492, and U.S.S.R., 172. Although a few countries that should be represented have failed to make the necessary returns, fifty-four are included, two more than in the first edition. An interesting addition is notes on the degrees awarded in several countries and their approximate equivalents. It may be anticipated that this list will prove even more useful than its predecessor and it is to be hoped that it will be found possible to continue the series at three-yearly intervals to coincide with the meetings of the International Union of Crystallography.

G. F. C.